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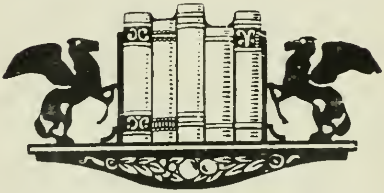

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THE NON-FERROUS METALS.

BY

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PREFACE TO THE FOURTH EDITION.

It has been a pleasant task to prepare, at the request of the Publishers, a new Edition of this well-known work of my old Professor, William Gowland. Since the Third Edition was published considerable advances have been made in many branches of Metallurgy, and the task of revision, although pleasant, has not been a light one.

Compared with the previous edition, the following may be mentioned as being the most important alterations or additions :

In the first section, dealing with refractory materials, minor alterations and additions have been made and a summary of the properties of silica at different temperatures has been included.

In the section on the metallurgy of copper, recent results showing the effects of foreign elements on the properties of the metal have been incorporated.

The pages dealing with the metallurgy of platinum have been largely re-written, owing to the developments in the treatment of platinum-bearing deposits taking place in South Africa.

An account of the extraction of cadmium from flue dust and bag-house fume, and from the precipitate obtained on electrolytic zinc plants, by wet methods, has been added, and the methods of treatment of tin ores have been largely re-written.

The final chapter on aluminium has been largely re-written in view of the advancement made in the metallurgy of this metal.

C. O. B.

Liverpool, *August*, 1930.

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PREFACE.

In the present volume an effort has been made to supply students and metallurgists with a concise treatise dealing with the principles on which the various processes which concern the non-ferrous metals are based, and with the manner in which the processes are carried out in typical modern works.

The general plan followed is to consider under the name of each metal (1) its physical and chemical properties; (2) the alloy of which it is the chief constituent; (3) the composition and applications of commercial brands, and the effects of substances which interfere with those applications; (4) the chief ores and the processes by which the metal is extracted from them or other sources, and refined or made suitable for industrial or other purposes; (5) the principles and conditions on which the success of these processes depend; (6) the furnaces and appliances employed in the processes, and the chemical changes and reactions which occur in the operations; (7) examples of actual practice followed at the present time in important extraction works.

Much that is not essential and processes which are obsolete have been omitted, while those which are falling into disuse are only briefly described.

In the chapters dealing with gold, silver, copper, and lead special care has been taken to keep pace with the progress which has been made in the metallurgy of these metals, and it is believed that no important modern successful process has been omitted.

Many of the illustrations are original, and a considerable number of the others have been selected from papers by well-known metallurgists, the sources in all cases being acknowledged.

The aim of the book is not only to help the student, but the author has also in view a wider circle than those merely who are going through a course of metallurgical training, and hopes that others who are actually engaged in practical work may find its pages worth consulting.

Much valuable information concerning the methods and appliances of modern metallurgical practice is, it is true, to be found in the technical periodicals and the proceedings of societies, but it is so scattered that for purposes of reference it is almost inaccessible to those whose time is limited or who have no technical library within reach, therefore, an endeavour has been made in this book to bring together under each of the metals treated the most important matter relating to the metal, so that it may be readily referred to by either students or practical metallurgists.

The author has taken special precautions to avoid errors, yet doubtless some may have escaped detection, he will, therefore, be obliged to anyone who may discover errors to kindly call his attention to them.

Great care has been taken to give in the text the source of each quotation and illustration, but special acknowledgment is due to the authors of *Rand Metallurgical Practice*, to the works of Collins (*Metallurgy of Lead*), Ingalls (*Metallurgy of Zinc*), Hofman (*Metallurgy of Lead*), Rose (*Metallurgy of Gold*), Peters (*Practice of Copper Smelting*), to the California State Mining Bureau, and to the proprietors of the *Engineering and Mining Journal*, the *Mining and Scientific Press*, the *Mining Magazine*, and *Mineral Industry*. The author has also to heartily thank Mr. T. A. Rickard, editor of the *Mining Magazine ;* Mr. Alfred James, of the Cyanide Plant Supply Company ; Mr. Walter M'Dermott, of Messrs. Fraser & Chalmers, for kindly supplying blocks for several of the illustrations.

WILLIAM GOWLAND.

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THE METALLURGY

OF

THE NON-FERROUS METALS.

REFRACTORY MATERIALS.

These are materials which resist exposure to high temperatures without melting or becoming markedly soft or pasty.

For many purposes it is also necessary that they should possess the property of resisting, as far as possible, the corrosive action of metallic oxides and of acid or basic slags.

They are used either raw or calcined or in the form of bricks for :—

1. The internal lining of furnaces, flues, and the hotter parts of chimney stacks.
2. For the soles, hearths, bottoms, roofs, and ports of furnaces.
3. For lining converters, ladles, and the like.
4. For the manufacture of crucibles.

Some estimations of the melting points of refractory bricks are described in Technologic Paper No. 10 of the Washington Bureau of Standards.

The following table summarizes the results obtained :—

Material.	Lowest Temperature of Flow. Degrees C.	Material.	Lowest Temperature of Flow. Degrees C.
Silica, . .	1,750	Alumina, .	2,010
Kaolin, . .	1,740	Magnesia brick,	2,165
Bauxite brick,	1,790-1,820 (some at 1,600)	Chromite brick,	2,050-2,180

No definite relation was established between the melting point and composition of any fire-clay bricks. Refractory materials may be conveniently divided into three classes, viz. :—

1. *Acid Refractory Materials.*—Materials consisting of SiO_2 or containing SiO_2 as their chief constituent or in excess of the bases present. They combine more or less readily with metallic oxides forming silicates, and are hence termed "acid." The most important are Dinas rock, ganister, quartz, quartzite, siliceous sandstone, chalcedony, and flint.

Most fire-clays, although generally considered neutral substances, contain unsaturated silica, and are to that extent acid.

2. *Neutral Materials.*—Materials which do not combine either with SiO_2 or basic oxides, as graphite and chromite, bone-ash (or its substitutes, p. 240).

3. *Basic Materials.*—These contain little or no free SiO_2, and resist well the action of metallic oxides. The chief are :—magnesite, magnesian limestone, lime, bauxite, and zirconia.

1. Acid Refractory Materials.—*Dinas Rock*, one of the most important acid refractory materials, is found at several places in South Wales.

It consists essentially of silica with very small proportions of alumina, iron, and lime, and occurs both in the form of rock and disintegrated like sand.

COMPOSITION OF DINAS ROCK.*

SiO_2,	97·0 to 98·3	CaO,	0·2
Al_2O_3,	1·4 ,, 0·7	Alkalies,	0·2
FeO,	0·5 ,, 0·2		

It is largely used for furnace bottoms and lining Bessemer converters after having been ground with a small proportion of lime or clay. Small amounts of these are essential as the material alone will not " bind "—*i.e.*, it is destitute of plasticity.

In the form of bricks it is even more extensively employed.

Dinas Bricks.—These bricks, which are called " Dinas " bricks or " silica " bricks, are made in the following manner :—The somewhat finely-ground rock is mixed with 1 to 3 per cent. of lime and a little water, and is pressed into iron moulds, like ordinary brick-moulds, by a lever press. As the brick is not strong enough to be handled in the usual manner, it is taken to the drying shed on the iron plate which formed the bottom of the mould. The floor of the drying shed is heated by flues below it. When dry the bricks are burnt in a circular kiln, covered by a dome, at the highest temperature possible, for 10 to 20 days. Clay is also used instead of lime as an addition in the manufacture of these bricks.

Dinas bricks were formerly coarse grained, the fracture showing irregular fragments of the rock imbedded in a magma of pale yellowish matter. The lime added had fluxed the surface of the fragments and so enabled them to form a compact mass. Finer grinding is now used for the best bricks.

COMPOSITION OF DINAS BRICKS.†

SiO_2,	96·80	CaO,	1·20
Al_2O_3,	0·92	Alkalies,	0·20
Fe_2O_3,	0·50		

For the commercial manufacture of silica bricks it was found best by Philippon ‡ to use material with at least 96 per cent. SiO_2, the precise form being unimportant so long as 30 per cent. of it is in impalpable powder and 70 per cent. in grains of 1 to 8 mm. diameter. The proportion of lime added was only 0·6 per cent. of the bricks. The bricks were fired at 1,300° C. in a tunnel kiln and were used for lining a Martin furnace. Chatelier and Bogitch § recommend a temperature of 1,400° C. for firing, provided it is maintained for a sufficiently great length of time. In any case they do not believe that there is any advantage in exceeding a temperature of 1,450° C.

According to A. Scott,‖ some American bricks examined by him contained only about 25 per cent. of unaltered quartz ; the average in five British bricks made by different firms was 45 per cent. The difference is due to the American bricks being burned at a higher temperature (Seger, cone No. 15, 1,435° C. and above), and for a much longer time than those made in this country.

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[*] Percy, *Fuel, etc.*, p. 147. [†] Harbord, *Steel*, p. 211.

[‡] Philippon, *Comptes Rendus*, 1917, pp. 1002-1005.

[§] *Trans. Am. Inst. Min. and Met. Eng.*, 1919, p. 160.

[‖] A. Scott, *Trans. Ceram. Soc.*, 1917.

Important researches have been carried out on the constitution of quartz, and many modifications are known to exist, of which eight are well known, their temperature ranges of stability being as follows :—*

Low-quartz, . .	Stable at temperatures up to 573° C.
High-quartz, . .	Stable from 573° to 870° C. ; capable of existence above 870°, but is then not the stable form.
Low-tridymite, . .	Capable of existence at atmospheric temperatures and up to 117° C., but is not the stable form over this range.
Lower-high-tridymite,	Capable of existence between 117° and 163° C., but is not the stable form over this range.
Upper-high-tridymite,	Capable of existence above 163° C., and is the stable form from 870° to 1,470° C. ; above 1,470° C. is again unstable ; melts at 1,670° C.
Low-cristobalite, .	Capable of existence at atmospheric temperatures and up to 200°-275° C., but is not the stable form over this range.
High-cristobalite, .	Capable of existence above 200°-275° C., and is stable from 1,470° to 1,710° C., the latter being its melting point.
Vitreous silica, . .	Capable of existence at atmospheric temperatures and up to 1,000° C. or above, where it begins to crystallize with measurable rapidity, but is an unstable undercooled liquid (a glass) at all temperatures below 1,710° C.

The expansion trouble met with in silica bricks is due to the changes from quartz to tridymite or cristobalite on heating, and is illustrated by the following table showing specific gravity and volume of one kilogram for the different varieties :—

Modification.	Specific Gravity.	Volume of 1 Kilogram.
Low-quartz, . . .	2·65	377 c.c.
Low-tridymite, . .	2·26	442 ,,
Low-cristobalite, . .	2·32	431 ,,
Vitreous silica, . .	2·20	454 ,,

For use in furnaces at temperatures above 870° C., the presence of quartz as such is undesirable because of the large expansion which takes place on passing from quartz to either tridymite or cristobalite ; this conversion, going on after the refractory material is in place, may cause permanent expansion, resulting in stresses in the structure, with possible breakage.

Silica bricks, although extremely hard and refractory, are not suitable for every part of a furnace. They should not be used—

1. For those parts where they would be exposed to cold draughts of air, as, for example, the lining of charging and fire-hole doors, air ports, etc.

2. For lining furnaces which are allowed to cool down frequently, as crucible furnaces for gold, silver, or brass melting.

3. For the lining or arches of annealing furnaces or roasting furnaces working at only moderately high temperatures. Under the above conditions the surface becomes disintegrated and flakes off. They are, however, eminently suitable for building the fire place, roof, sides, and fire bridge of nearly all furnaces in which a high temperature prevails.

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* R. B. Sosman, *The Properties of Silica.* The Chemical Catalog Company, 1927.

In copper-smelting and refining furnaces they resist not only the high temperature, but also the corrosive action of slags, even when these are decidedly basic, very much better than any fire-clay bricks. They are, however, unfit for use in a basic open hearth except for the roof and the upper parts of the sides.

Kieselguhr is a highly siliceous material left by the decay of diatoms, and it is used to some extent for manufacturing very porous bricks of a low specific gravity, useful where insulation without great strength is desirable.

Ganister.—Strictly speaking, "ganister" is the name of a siliceous rock found in the lower coal measures of South Yorkshire, largely worked in the neighbourhood of Sheffield, but is now often used as a generic term for any similar material wherever found, also for artificially prepared mixtures of silica rock with clay.

Welsh ganister, which is of the latter kind, is a siliceous rock, mixed with small quantities of lime. It is very refractory, but for fettling copper furnaces it does not "bind" so well, in the author's experience, as Sheffield ganister.

Sheffield ganister is often plastic, to some extent, when simply ground and mixed with the necessary amount of water. It is, however, usually ground together with fire-clay in various proportions, according to the purposes for which it is required, rather more clay being used when it is intended for fettling than for furnace bottoms or silica bricks.

COMPOSITION OF GANISTER.*

SiO_2,	92·05	94·60	95·20
Al_2O_3,	2·70	1·40	0·59
Iron oxide,	1·85	0·90	0·74
CaO,	0·60	0·48	0·40
MgO,	0·20	0·16	0·16
Alkalies,	0·20	0·14	0·18
Water,	2·00	2·60	2·70

Ganister bricks are made in the same manner as Dinas bricks, the raw material either being used alone or mixed with a small proportion of fire-clay.

In setting silica or ganister bricks the same material as that of which the bricks consist should always be employed.

Quartz, Quartzite, Chalcedony, and Flint.—SiO_2 in one or other of these forms will often be found as gangue, or in association with mineral veins.

These materials, although they cannot be used raw, are most valuable for the manufacture of silica bricks and furnace sand when suitably treated. In the manufacture of bricks and refractory sand from these substances the author has found the following method to be satisfactory :—

1st. Calcine at a red heat in a reverberatory furnace, or in stalls, until the lumps are thoroughly broken up. Rake out of the furnace and quench with water.

2nd. They can now be easily ground with 1·5 to 3 per cent. of lime, or rather more fire-clay, under edge rolls or in a pug-mill, to proper degrees of fineness for sand or bricks.

The bricks are made as described under "Dinas bricks," p. 2.

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* Harbord, *Steel*, p. 13.

Siliceous Sand.—This material is in extensive use for the working bottoms of furnaces in copper smelting. If the sand be required to resist very high temperatures, it should contain not less than 95 per cent. SiO_2, not more than 4·0 per cent. Al_2O_3, nor more than 1·0 per cent. CaO. Preferably, as a rule, 98 per cent. SiO_2 should be present for steel work, but some good sands contain 1 or 2 per cent. less. The size of grain is important, it should not be too coarse or too fine.

For somewhat lower temperatures a sand containing less SiO_2 may be employed as for the bottoms of the reverberatory furnaces in which the operations of smelting and refining are effected in copper-works.

COMPOSITION OF THE SAND USED FOR THE BEDS OF COPPER FURNACES AT SWANSEA.*

	Weston.	Le Play.
Silica,	87·87	86·0
Alumina,	2·13	1·6
Peroxide of iron,	2·72	1·2
Lime,	3·79	5·7
Magnesia,	0·21	0·8
Carbonic acid and a little water,	2·60	4·5
	99·32	99·8

The source of the lime was the intermixed shell substance, which consists almost wholly of carbonate of lime. At a high temperature the lime would, as in the case of Dinas brick, tend to cement the siliceous particles of the sand together. Hence the suitableness of the sands in question for copper-furnace bottoms is probably due to the presence of calcareous matter. This sand is, however, much inferior to ganister for furnace bottoms.

Sandstones rich in SiO_2 may also be used for the refractory lining of furnaces. Soapstone, serpentine, and gneiss are also in use in some countries. Whatever kind of stone be used, if in blocks, it should be stored for a considerable time in a warm place in order to dry it perfectly.

When stratified rocks are employed the blocks should be built into the sides of the furnace in accordance with their natural bedding.

Silicon carbide in various forms such as Carborundum, Crystolon, Silfrax, Silit, Silundum and Siloxion, which are products of the electric furnace, is used as refractory material where high temperatures and reducing atmospheres have to be withstood.

Fire-clays.—These are clays possessing refractory properties in a high degree. Fire-clays are usually classed as neutral refractory materials ; but, as has been already pointed out, they are not really neutral, but occupy a position intermediate between the more markedly acid and the true neutral substances. This will be evident when we consider the composition of the purest form of clay (kaolinite, Al_2O_3, $2SiO_2 + 2H_2O$)—SiO_2 46·33 per cent. ; Al_2O_3 39·77 ; H_2O 13·9. In fire-clay generally, however, the SiO_2 ranges from 50 to 65 per cent. or more, and the Al_2O_3 from 22 to 35 per cent.

Fire-clays may hence be generally regarded as mixtures of pure clay, kaolinite (hydrated aluminium silicate), with excess of silica and small quantities of earthy and other silicates.

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* Percy, *Fuel, etc.*, p. 152.

This excess of silica up to a certain percentage diminishes but above it increases the refractory properties.

The plasticity of fire-clays, which depends on the combined water they contain, is increased by weathering, and at the same time their refractory properties are increased to a certain extent.

Composition of some Typical Fire-clays.

	Stannington. For Steel Pots. (Percy.)	Glenboig. (Riley.)	Stourbridge. For Glass Pots. (Tookey.)	Dowlais. Considered good. (Riley.)	Ireland. Very refractory. (Henry.)
SiO_2, . . .	48·0	56·42	63·30	67·12	79·40
Al_2O_3, . .	34·5	26·40	23·30	21·18	12·25
Iron oxide, .	3·5	1·33	1·80 (FeO)	1·85(Fe_2O_3)	1·30(Fe_2O_3)
CaO, . . .	0·7	0·60	0·73	0·32	0·50
MgO, . .	..	..	..	0·82	..
Alkalies, . .	..	..	..	2·02	..
Water and organic matter, . .	11·0	13·75	10·30	7·21	5·20

Fire-clays of excellent quality are of extensive occurrence in the coal measures in this country, while fairly good fire-clays may also often be found in layers of varying thickness in the low hills of detritus at the base of granitic mountain ranges. They require to be carefully selected, as mica and alkalies are liable to be present in injurious proportions.

The substances found accompanying fire-clays, and in a state of more or less intimate admixture with them, are—iron oxides, calcium carbonate, iron pyrites, alkalies, titanium compounds, mica, and sand, all of which tend to lower the refractory properties. Iron oxides, as a rule, should not be present in more than small proportions. According to Snelus, up to 2 or 3 per cent. they do not seriously lower the refractory properties of a clay if the alkalies be present in only small amounts. Much depends, however on the nature of the oxide present. If as Fe_2O_3 (ferric oxide) a fire-brick may contain the above amounts or even more and be very refractory when used for furnaces in which the atmosphere is oxidising, as Fe_2O_3 and SiO_2 do not combine ; but if the same brick be used for furnaces where the atmosphere is reducing, the Fe_2O_3 would be reduced to FeO, which would combine with the SiO_2 forming a fusible silicate, and the brick would be destroyed.

Calcium carbonate, if in small pieces, will cause local corrosion in fire-bricks or crucibles, while if uniformly diffused through a fire-clay in the proportions usually found it has no deleterious effect.

Particles of iron pyrites cause great local corrosion. Alkalies are most injurious, seriously increasing the fusibility of clays. Two per cent. should be the maximum permissible. Titanium compounds are frequently present in fire-clays, but the amount present (under 2 per cent.) has little effect on the refractoriness. Mica is similar, but much less powerful in its effects.

Fire-bricks.—The term fire brick is commonly applied to bricks made of fire-clay, other bricks being usually designated by prefixing the name of the material of which they are composed, or its nature, thus, for example, we have silica bricks, basic bricks, etc.

The qualities required in fire-bricks have been well stated by Dr. Percy as follows :—

1. " They should not melt, or soften in a sensible degree, by exposure to intense heat long and uninterruptedly continued.

2. " They should resist sudden and great extremes of temperature.

3. " They should support considerable pressure at high temperatures without crumbling.

4. " They may be required to withstand, as far as practicable, the corrosive action of slags rich in protoxide of iron or other metallic oxides."[*]

The fire-clay is ground and mixed with water to give the necessary consistence for the making of bricks, burnt clay being added at some works, especially when slabs or fire-tiles are being made. The bricks are made by hand, the moulds being of bronze set on a plate covered with felt, except where the nameplate is fixed. After a mould has been filled the excess of clay is removed by means of a " smoothing board." The bricks are taken to an iron drying floor where they are set on edge, and when dry they are fired in kilns.

The following analyses of high-class fire-bricks by Mr. J. E. Stead are taken from Harbord's *Steel*, p. 267.

ANALYSES OF FIRE-BRICKS.

	Silica, SiO_2.	Alumina, Al_2O_3.	Oxide of Iron, Fe_2O_3.	Lime, CaO.	Magnesia, MgO.	Potash, K_2O.	Soda, Na_2O.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Wortley, Leeds,	72·65	23·75	1·75	0·30	0·36	0·81	0·29
Stourbridge, .	69·00	27·30	1·86	0·27	0·32	0·65	0·26
Glenboig, . .	63·00	32·00	2·85	0·79	0·36	0·74	0·20
Newcastle, .	60·10	34·65	1·89	0·52	0·38	2·05	0·35
Durham (Newfield),	65·40	27·56	2·00	1·12	0·72	2·12	0·34
Derbyshire calcined fire-clay,	68·05	27·50	2·01	0·35	0·68	1·08	0·34

These fire-bricks are in extensive use for—

1. The construction of all furnaces and parts of furnaces where silica or other special bricks are not required.

2. The linings of large and small blast furnaces for smelting iron, copper, lead, and other metals.

3. The construction of reverberatory furnaces, working at lower temperatures than for copper smelting, such as annealing, roasting, softening, reheating, and similar furnaces ; and of coke ovens.

4. Crucible furnaces for melting gold, silver, copper alloys, etc.

5. The linings of flues and chimney stacks.

6. The chequer work of regenerative furnaces.

Agalmatolite.—Chinese figure stone. Usually seen in this country in the form of grotesque figures and ornaments.

It is an indurated clay, and occurs in vast deposits in China and Japan.

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[*] Percy, *Fuel*, p. 144.

The author has used it largely for making fire-bricks for crucible furnaces for melting gold and silver in the Imperial Japanese Mint. It is a rock of moderate hardness, but when finely ground and mixed with water is quite plastic, and in spite of the amount of potash (5 to 6 per cent.) which it contains, it makes an excellent fire-brick for moderately high temperatures.

Composition, SiO_2 54·50 ; Al_2O_3 34·00 ; FeO 0·75 ; K_2O 6·25 ; H_2O 4·0.

2. Neutral Refractory Materials.—*Graphite or Plumbago.*—An allotropic form of carbon, usually containing more or less earthy matter consisting of silica and alumina, with smaller proportions of iron oxide and lime.

Graphite is one of the most valuable materials for the manufacture of crucibles, as it neither melts nor softens at the highest temperatures of furnaces, neither does it undergo any change if air be excluded, and even when exposed to the action of air, as in air furnaces, it is but slowly burned.

There are two well-defined trade classes—viz., the " crystalline " and the " amorphous." The former is the most important to metallurgists, as it is specially suitable for crucibles on account of its flaky structure which counteracts any tendency to cracking.

The amorphous is used for facings, paint, stove polish, etc. It is unsuitable for crucibles, as when used in their manufacture they are too close grained in texture and liable to crack.

In the selection of a graphite for the manufacture of crucibles the following are the chief points to be considered :—

1. The percentage of carbon.
2. The texture, which must be flaky.
3. The percentage of iron, which should be low.
4. The amount and composition of the ash. This is of considerable importance.

As graphite is not plastic a certain proportion of clay must be mixed with it for the manufacture of crucibles, hence the percentage of ash should not be high, and its constituents should not form easily fusible compounds with the fire-clay added.

The ash varies from about 3 to 30 per cent. or more, and consists usually of SiO_2 and Al_2O_3, with smaller proportions of iron oxides and a little lime.

If too much iron oxide be present the graphite is treated with sulphuric acid in leaden tanks for its removal.

Ferguson * describes the requirements for crucible graphite as follows :— " Graphite for the making of crucibles must be of great purity. Its content of graphite carbon should exceed 85 per cent., and preferably should be as high as 90, and it must be practically free from mica, pyrite, and iron oxide. A small amount of quartz is not injurious. Graphite for making crucibles should also be coarse enough for the interlocking fragments to be bound by the clay with which it is mixed. It should contain a large percentage of flake about 1 mm. in diameter, and should all remain on a 100-mesh screen."

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* H. G. Ferguson, *U.S. Geological Survey*, 1918, p. 97.

Dub * recommends the following specification for No. 1 flake graphite :—At least 85 per cent. of carbon remaining after the dried sample has been burned for three minutes at 800° C., the particles should have less than 3 per cent. residue on a No. 35 standard screen, less than 50 per cent. on a No. 65 standard screen, and should remain completely on a No. 100 screen.

American consumers of crucible graphite, with one exception, maintain that American flake will not make a good crucible of itself, not having the proper physical formation, and that 25 to 30 per cent. of it is all that can be successfully used in mixture with the Ceylon product.

Ceylon affords the chief supply of "crystalline" graphite, and no graphite from any other locality is a satisfactory substitute. Other countries producing it are the United States (especially Alabama), Austria, Madagascar, Italy, Germany (Bavaria), Canada, Czechoslovakia, Russia, and Korea.

Graphite deposits occur widely distributed in Korea; they are, for the most part, of rather low grade and of the amorphous kind. True crystalline graphite occurs, however, but the extent of the deposits has yet to be ascertained.

Selected specimens of graphite from Ceylon, the United States, and Canada may contain 99·7 to 99·8 per cent. of carbon, but generally will range from 70 to 90 per cent.

Chromite (*Chrome Iron Ore*, Cr_2O_3FeO).—Chromite frequently contains considerable amounts of Al_2O_3 and MgO, with CaO in smaller proportions.

The following are typical analyses of the ore :—

CHROMITE ORES.

	Turkish.†	New Caledonian.†	Locality not given.‡	California.
Cr_2O_3, . . .	51·70	55·70	51·54	52·68
FeO, . . .	14·20	16·60	35·82	15·30
Al_2O_3, . . .	14·10	18·20	3·01	11·40
MgO, . . .	14·30	9·80	2·60	16·23
SiO_2, . . .	3·50	0·25	2·25	3·40
CaO, . . .	1·70	0·25	4·20	..
MnO, . . .	..	0·20	..	0·15
P_2O_5, . . .	..	0·05	..	..
H_2O, . . .	0·30	1·05	..	0·94

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* G. D. Dub, *Bureau of Mines War Min. Inv. Ser.* 3, pp. 20-21, December, 1918.

† *Eng. and Min. Journ.*, Oct. 1908.

‡ Harbord, *Steel*, p. 212.

Chromite should contain not less than 40 per cent. of Cr_2O_3 and not more than 5 per cent. of SiO_2. It is then practically infusible at furnace temperatures, and is not acted on by siliceous slags.

Chromite is made into bricks by grinding it, mixing with lime, and the necessary water, moulding in metal moulds like silica bricks, and burning in kilns at a very high temperature. The bricks are used for lining the settlers at several important copper works, for the crucibles of blast furnaces smelting refractory lead ores, and for forming the boundary courses between the basic and the silica bricks in the sides of basic open-hearth steel furnaces. It would be an excellent material for the fire-bridges of reverberatory furnaces for copper smelting and refining.

The use of chromite bricks, however, for the complete linings or bottoms of reverberatory copper furnaces has the following great disadvantages :—They largely absorb copper and silver, and the cobbing obtained by breaking up saturated bricks cannot be smelted at any temperatures obtainable in copper furnaces. At Silverspur (Australia), when smelting a high-grade matte, even the cleaner pieces of chromite assayed over 30 ozs. of silver per ton.*

The most valuable deposits of chromite are found in Southern Rhodesia, New Caledonia, India, Turkey and Russia.

Bone Ash.—Calcium phosphate containing about 10 per cent. of calcium carbonate. It is prepared by calcining bones. Formerly it was almost exclusively employed in the manufacture of pottery and for making cupels for assaying, and the " tests " used in the cupellation of argentiferous lead ; but during recent years other materials have been substituted for it (see " Lead," p. 240).

3. Basic Refractory Materials.—They contain but little or no SiO_2, and resist well the action of metallic oxides. Those in common use are lime, dolomite, magnesite, and bauxite.

Lime is practically infusible. It is obtained by driving off the CO_2 from limestone by burning in kilns. It is, however, difficult to make use of it as a refractory material for furnaces owing to its property of readily combining with water, when it swells up and falls to pieces.

It has been used after having been made into bricks with tar, but the bricks so made are very inferior to those of magnesian limestone similarly prepared. It has also been used in the form of blocks for small furnaces for melting platinum.

Dolomite (*Magnesian limestone*).—A double carbonate of Mg and Ca, $MgCO_3 . CaCO_3$. It contains 45·7 per cent. $MgCO_3$, but is rarely pure. In steel works the term is applied to magnesian limestone, in which the proportion of magnesium carbonate varies greatly, and is always less than in dolomite proper.

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* E. Hall, *Eng. and Min. Journ.*, February, 1916.

This material is very extensively employed, after being burnt, for lining basic Bessemer converters, and for the linings and hearths of basic open-hearth furnaces, for the manufacture of steel. The burnt product consisting of MgO and CaO has no binding power, it is therefore ground and mixed with pitch or anhydrous tar, the mixture being used either direct or after being made into bricks.

The dolomite usually employed contains before burning about 18 to 20 per cent. MgO, and 28 to 32 per cent. CaO, with small proportions of Al_2O_3 and FeO.

It should not contain less than 18 per cent. MgO, nor more than 2 per cent. SiO_2, although, in some localities, dolomites containing rather less MgO and more SiO_2 are employed. At Middlesbrough as much as 6½ per cent. SiO_2 is sometimes present.

In the following table are given analyses of typical dolomite :—*

DOLOMITE.

Raw.			Calcined.		
SiO_2, . .	1·10	0·90	SiO_2, . .	3·66	2·50
FeO and Al_2O_3,	1·64	1·30	Fe_2O_3 and Al_2O_3,	4·80	3·99
CaO, . .	33·20	31·00	CaO, . .	55·50	57·32
MgO, . .	19·60	20·60	MgO, . .	34·83	34·75
CO_2, . .	44·30	46·34	Loss in ignition,	1·06	1·00

"Shrunk" dolomite, as the calcined material is termed, is dolomite burnt at a very high temperature in a cupola furnace using a blast of about 16-oz. pressure with coke as fuel. It is ground as soon as possible in a pug mill until the larger lumps are not bigger than peas, and then mixed with the required amount of well-boiled hot tar, often in the same mill. The product is then either used in this form or is moulded into bricks or blocks in a hydraulic press.

In the United States dolomite is usually burned in rotary kilns, oil-fired, and is liable to slake readily if the temperatures have not been sufficiently high.

Magnesite (*Magnesium Carbonate*, $MgCO_3$).—Magnesite generally contains iron oxide, lime, alumina, and silica. In the Table which follows are given analyses of several kinds :—

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* Harbord, *Steel*, p. 212.

MAGNESITE.

	1. Greek.	2. Greek.	3. Styrian.	4. Styrian.
$MgCO_3$, . .	95·12	93·70	90 to 96	42·70 MgO (89·67 $MgCO_3$)
$CaCO_3$, . .	4·02	4·02	0·5 ,, 2·0	1·82 CaO
Iron oxides, .	trace	0·07	3 ,, 6	} 4·40
Al_2O_3, . .	..	0·10	..	
SiO_2, . .	0·52	2·20	0·1	0·92
H_2O, . .	0·34	..	..	..
Loss on ignition,	..	..	..	50·01 CO_2

1. *U.S. Consular Report*, Feb. 1900.
2. *Journ. Soc. Chem. Ind.*, 1900, p. 503.
3. Havard, *Refractories and Furnaces*, p. 90.
4. Harbord, *Steel*, p. 212.

Magnesite is one of the most valuable basic materials. For metallurgical uses it must be " dead burnt " by calcining it at 1,700° C. in a cupola driven by a blast. Electrically sintered magnesite is produced in quantity by the Carborundum Co. of Niagara Falls. It shows no contraction when put into use and has a melting point of 2,600° C. Properly calcined magnesite is practically infusible, has no tendency to absorb water, and does not readily combine with silica when used in furnace linings. For the last reason, in addition to its infusibility, it is used for the boundary courses between the dolomite and the silica bricks in basic open-hearth steel furnaces. It is also used for the hearths and linings of these furnaces, but its employment for this purpose is limited by its high cost as compared with dolomite. During recent years it has come into extensive application for the linings of basic converters for the Bessemerizing of copper mattes.

In all these cases it is used in the form of bricks, which are prepared as follows :—The dead-burnt magnesite is ground, mixed with the necessary amount of water, moulded and burnt at a very high temperature like silica bricks. Magnesite calcined at 800° C., tar, etc., are sometimes used as binding materials.

The most important deposits of magnesite are found in Austria, Russia, United States of America, Greece and India.

Bauxite.—Hydrated oxides of aluminium and iron with some silica and often titanium oxide. The relative proportions of the Al_2O_3 and Fe_2O_3 and also of the SiO_2 vary greatly, and only those kinds in which the two last are present in low percentages are suitable for the manufacture of the most refractory bricks. There are two kinds of bauxite—viz., the red and the white.

The average red bauxite mined in France contains Al_2O_3 54 to 65 per cent., Fe_2O_3 19 to 28 per cent., SiO_2 1 to 5 per cent., and FeO 2 to 3 per cent., and is the chief source of supply for the manufacture of aluminium.

The white bauxite, which is used for making refractory bricks, contains Al_2O_3 45 to 47 per cent., Fe_2O_3 traces, and SiO_2 up to 28 per cent.*

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* *Min. Ind.*, 1909, p. 70.

For the best bricks, however, the proportion of SiO_2 should not exceed 6 or 8 per cent.

For the manufacture of bricks the bauxite is ground, and washed, if necessary, to remove some of the free silica. It is then calcined in a rotary kiln at a temperature of about 1,400° C., using oil, gas, or coal for the fuel, then mixed with clay as a " binder," and moulded into bricks which are burnt at a high temperature.

The bricks are liable to considerable shrinkage at very high temperatures. They resist well the action of metallic oxides, and are hence used for lining open-hearth furnaces, but are not in common use for that purpose. They are also used for the upper courses of lead-softening and refining furnaces.

Burnt bauxite is employed in some works in Germany, in admixture with clay or lime, for lining Bessemer converters.

France is the chief producer of bauxite, but large deposits are also worked in Hungary, the United States (especially in Arkansas), Jugoslavia, and in British and Dutch Guiana.

High-grade bauxites are now under development in the Central Provinces, India.

Alundum or Corundum is made by fusing bauxite or prepared alumina in an electric furnace. It is mixed with fire-clay for the manufacture of crucibles, these having a high melting point, 2,000° C., a low coefficient of expansion, and a heat conductivity about three times that of firebrick.

Zirconia (ZrO_2).—Zirconia which until recent years was considered one of the rare oxides, is now being supplied in commercial quantities and used on an industrial scale.

It is one of the most refractory substances yet known, neither alkalies nor molten silicate slags attack it, nor is it attacked like graphite by the oxygen of the atmosphere.

When pure its fusing point is in the neighbourhood of 3,000° C., and according to E. H. Rodd,* even when containing about 1·25 per cent. SiO_2 and Fe_2O_3, it does not melt below 2,560° C.

The chief source of zirconia is an ore which occurs in large quantities in Brazil. Other localities are Ceylon, Australia, the Ural Mountains, and North America, but these so far are of little importance.

The zirconite mineral found in Brazil is a mixture of brazilite, zircon, and a new unnamed zirconian silicate. Its trade name is registered as " zirkite."

The mean of three analyses † of an average sample was as follows :—

ZrO_2,	84·1
Fe_2O_3,	3·1
SiO_2,	7·74
TiO_2,	1·21
Al_2O_3,	0·66
Loss on ignition,	2·72

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* E. H. Rodd, *Journ. Soc. Chem. Ind.*, 1918, p. 214 R.

† H. Conrad Meyer, *Met. and Chem. Engineering*, 1915, vol. xiii., p. 257.

Tests made on the mineral by G. T. Stowe at the Ohio State University by grinding it to 100-mesh and moulding into cones showed no fusion at Cone 35 (1,830° C.).*

A satisfactory commercial process for the manufacture of zirconia bricks † of the highest refractory power consists in grinding the crushed ore to about 60-mesh in a dry pan. All particles finer than 100-mesh are removed, and the coarser material is mixed with an equal weight of the finely water-ground ore made into a stiff paste and moulded in the same manner as silica bricks. (The percentage of loss due to cracked and warped bricks is rather high, but the damaged pieces may be re-ground.)

Other bonding materials have been used, magnesium chloride, sodium silicate, and water-free tar, but the best is the very finely ground ore.

The initial cost of a zirconia furnace lining, which is rather high as compared with, for example, magnesite, is more than compensated for by its high melting point, high resistance to corrosive slags, metals and metallic oxides, and by its low thermal conductivity.

It has been found that a zirconia-lined hearth of an open-hearth steel-making furnace at Remschied was still in good condition after four months' continuous working at high temperatures. Calculations based on the same tests showed in actual maintenance costs a saving of more than 50 per cent. in favour of zirconia, as compared with the refractory lining ordinarily used.‡

Crucibles.—The term crucible is generally applied to open-mouthed vessels in which metals or other materials are heated in furnaces, and which can be handled by tongs or other means. In the more technical sense, the term is also applied to the hearth of a blast furnace.

The qualities required in ordinary crucibles have been admirably stated by Dr. Percy § as follows :—

" They should all resist a high temperature without melting or softening in a sensible degree, and should not be so tender, while hot, as to be liable to crumble or break when grasped with tongs.

" In some cases they should resist sudden and great alterations of temperature, so that they may be plunged while cold into a nearly white-hot furnace without cracking, while in other cases it is only necessary that they should resist a high temperature after having been gradually heated.

" They may occasionally be required to withstand the corrosive action and permeation of such matters as molten oxide of lead.

" In special cases, the material of which they are composed must not contain any ingredient that would act chemically upon the substances heated in them ; thus, carbonaceous matter should not be one of their constituents when they are used in the heating of such oxidized matters, as carbon would reduce, and reduction is not desired."

Earthen or Clay Crucibles.—These crucibles are made of a mixture of fire-clays, together with burnt clay (grog), silica, or other refractory material, the first-named being most generally employed.

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* H. Conrad Meyer, Paper read at Meeting of the Ceramic Society held at Swansea, 1918.

† *Ibid.*

‡ *Nature*, May, 1917, p. 375.

§ Percy, *Fuel*, p. 110.

These latter materials must, as far as possible, resist fusion at high temperatures, and must also have the property of counteracting the contraction to which clay crucibles are liable when strongly heated, and which tends to induce cracking. They also act the part of a rigid skeleton and thus prevent the collapse of the crucible in the furnace. Old crucibles and glass pots, free from slag, and ground to a proper degree of fineness, are a satisfactory material.

The exact proportions of burnt clay to be used can only be decided by experience; they range from 1 part of burnt to 2 parts of raw clay, to 2 of burnt to 1 of raw. The fineness to which the grog must be ground also varies. The author has made excellent scorifiers from a mixture of 2 parts, by measure, of Stourbridge fire-clay with 1 part of ground Stourbridge fire-bricks, slightly moistened with water, and pressed in an iron mould in a hydraulic press.

There are many kinds of crucibles, and formerly each kind was made in a special locality—for example, there were Cornish, London, triangular Hessian, French fluxing pots, etc. The Morgan Crucible Co., Battersea, manufacture each type of crucible.

As a rule, crucibles are usually purchased from crucible manufacturers, except for crucible steel making, when they are made in the works. In remote districts, and under special circumstances, they may occasionally, however, have to be made locally. In such cases, the following will be found to be satisfactory methods, although the crucibles made will often not be equal in quality to those from crucible manufacturers.

A suitable fire-clay should be obtained, if possible. The following Table of analyses of well-known crucibles will aid in the selection of a clay and the preparation of a proper mixture :—

Analyses of Crucibles.

	Cornish. (Percy.)	Hessian. (Berthier.)	French Beaufay's. (Berthier.)	French Deyeux's. (Berthier.)
SiO_2, ...	72·39	70·9	64·6	72·3
Al_2O_3, ...	25·32	24·8	34·4	19·5
Fe_2O_3, ...	1·07	3·8	1·0	3·9
CaO, ...	0·38	..	..	..
K_2O, ...	1·14	..	..	..
MgO, ...	trace	trace	..	..

Crucibles for assaying are best made in a cast-iron mould, the interior of which is of the shape and size of the crucible to be made, with an iron or wooden plug or core of the shape and size of the interior of the crucible. Within the mould at the bottom is a loose circular plate of iron. The top of the mould is furnished with a cover with a central hole to form a guide for the plug.

A lump of the clay mixture is placed in the mould, the plug introduced and forced home by a heavy hammer. The plug is then removed, and the crucible pushed out by means of the iron plate.

Larger crucibles to be used as melting pots may be made as follows :—

The pot is moulded by hand on a wooden core of the requisite shape and size. In the bottom of the core is fixed an iron spindle which works in a hole on the working bench, so that the core can be revolved. A cap of wetted linen or calico is placed on the core, and upon this the clay is moulded by hand to the proper thickness as determined by a vertical gauge. During the moulding the clay must be beaten with a wooden bat to give the necessary compactness to the sides of the pot. When the pot is finished the whole is lifted out of the socket in the bench, inverted, and with a little coaxing the pot drops off. The pots must be very slowly dried before being used. The fire-clay employed in making them should be "tempered" by exposure to the weather for a considerable time, and the burnt clay which is mixed with it should be thoroughly incorporated by treading or in a pug-mill. If after they have once been used, they are allowed to become cold, they crack and are worthless.

Large fire-clay crucibles are, however, but little used now, except in crucible-steel works, as liners for plumbago crucibles in Miller's parting process, and in melting the gold slime from the zinc boxes in the cyanide process.

Graphite, Black Lead, or Plumbago Crucibles.—Plumbago crucibles have almost entirely replaced fire-clay crucibles, except in the cases just mentioned.

They are manufactured on a very extensive scale in this country by the Morgan Crucible Company, Battersea, and in the United States by the Dixon Crucible Company, New Jersey.

The graphite employed in the manufacture of these crucibles must be flaky in structure, and as it is not plastic it has to be mixed with refractory clay in suitable proportions to enable it to be moulded. The mixture is best effected by a pug-mill.

Good plumbago crucibles should possess the following properties :—"They support, even when of the largest size, the greatest and most sudden alterations of temperature without cracking ; they may be used after having been repeatedly heated and cooled, so long as they are not too much reduced in thickness by the burning away of the graphite to bear the weight of the metal, which may be melted in them, and to admit of being held by tongs without breaking ; their surface within should be smooth, so that the particles of melted metal may not hang about the sides." * The graphite on the outer surface gradually burns away, but this loss may be reduced by dipping them in a cream of fire-clay to which a little borax has been added.

They do not stand the action of fluxes well, hence when these have to be used, bone-ash must be thrown in from time to time, so that a ring of this material may be formed around the edge of the metal to absorb them, together with any oxides which may be formed.

English plumbago crucibles contain about 48 per cent. of carbon as graphite.

In America the mixture employed in their manufacture consists of Ceylon graphite about 50 per cent., air-dried clay 45 per cent., and sand 5 per cent.* The proportion of clay to sand varies with different makers, some using 41 to 43 per cent. of the former and 7 to 9 per cent. of the latter.

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* Percy, *Fuel*, p. 122.

They are moulded either on a potter's wheel, or by machinery in moulds of plaster of Paris and then very carefully dried. and afterwards burnt in saggars in kilns.

Plumbago crucibles should be stored for some time on shelves in the melting room, and before using they require to be carefully annealed as follows :—At the end of the working day the fire in each furnace should be allowed to burn down, some cold coke is then thrown in and the crucible placed with its mouth downwards upon it and covered with fresh coke. The fire is then left to burn up very slowly until the crucible is red-hot. It can then be placed upright in the furnace to receive the charge of metal.

The Salamander crucibles of the Morgan Crucible Company are plumbago crucibles, which are covered with a waterproof glaze to prevent absorption of moisture and to render annealing unnecessary.

Silica Crucibles.—Vitreous silica is largely used for the manufacture of laboratory crucibles and other apparatus. It is made in two distinct grades —viz., transparent vitreous silica, which is free from bubbles and striæ and is made by fusing selected quartz crystals ; this variety is often known as "fused quartz." The second variety is opaque vitreous silica, often called "fused silica" or "Vitreosil"; it is full of small gas bubbles which are drawn out into tubes in the process of shaping, the product sometimes having a silky appearance on this account; this variety is either opaque or only translucent, and is made from quartz sand or some other finely divided form of quartz. Electric resistance furnaces are used for the fusion of the quartz on a large scale. The final shape of the various articles is obtained by extrusion, drawing or blowing while the material is sufficiently hot to flow.

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* Howe, *The Metallurgy of Steel*, p. 299.

ROASTING.

Roasting furnaces are those in which ores or metallurgical products, either alone or with the addition of other materials, are subjected to the action of heat, or of heat and air, at temperatures below their melting points, in order to effect chemical or mechanical changes in them that will facilitate their treatment in subsequent operations.

The process of roasting may be classified according to the objects to be attained as follows:—

1. Calcination.
2. Oxidizing-roasting.
3. Blast-roasting.
4. Chloridizing-roasting.
5. Sulphating-roasting.

1. *Calcination.*—This term is frequently used as a synonym of "roasting," but should be confined to those operations in which matter is simply expelled, or the physical structure altered by the application of heat alone.

Examples.—Heating limestone, dolomite (p. 11), or calamine (p. 465), for the expulsion of CO_2; and iron ores to expel water and increase their permeability to reducing gases in the blast furnace.

2. *Oxidizing-Roasting.*—The most common form of roasting by which, through the combined action of heat and air, sulphur, arsenic, antimony, etc., are expelled from their compounds with metals and the metals converted into oxides.

Examples.—Heating galena, pyritic copper ores, zinc blende, arsenical and antimonial ores, with the admission of atmospheric air (see pp. 192 and 71).

3. *Blast-Roasting.*—An oxidizing-roasting in which air is forced through the ores or mattes, contained in suitable apparatus, for the expulsion of sulphur and oxidation of the metals.

Examples.—The blast-roasting of galena and pyritic copper ores and mattes (see pp. 195 and 73).

4. *Chloridizing-Roasting.*—The conversion of a metal or compound of a metal into a chloride by heating with common salt, with the admission of air.

Examples.—Silver ores are thus treated when they contain sulphide, sulpharsenides, and sulphantimonides of silver, in order that Ag may be converted into AgCl to render them amenable to treatment by amalgamation, or by Patera or other lixiviation methods (see pp. 390-415).

5. *Sulphating-Roasting.*—This is a partial oxidizing-roasting in which part of the sulphur only is expelled, the remainder being oxidized to SO_4.

Examples.—Argentiferous copper matte is thus treated in order to convert the silver into sulphate, so that it may be leached out with hot water in the Ziervogel process (see p. 419); also zinc blende for conversion into $ZnSO_4$.

Calcination.—On a large scale the process is chiefly confined in the metallurgy of the non-ferrous metals to the treatment of calamine, dolomite, magnesite, and bauxite.

In the case of calamine, the process is carried out in kilns, reverberatory furnaces, and revolving cylinders with continuous discharge (see "Zinc," p. 466). It is frequently practised at mines before shipment in order to reduce the weight of the ores, and thus lessen the cost of transport. Dolomite requires such high temperatures for calcination that kilns or ordinary roasting furnaces cannot be used, hence the operations have to be performed in cupola furnaces with coke as fuel (see p. 11).

In the calcination of bauxite a high temperature is also required, but not higher than can be attained in a rotary cylindrical calciner such as is used in the manufacture of hydraulic cement.

Oxidizing-Roasting.—The ores to be roasted may be either in the form of lumps or more or less fine powder, each class requiring different treatment.

Roasting of Ores in Lumps.—This may be carried out in piles or heaps, in stalls or in kilns.

Heap-Roasting.—Formerly in extensive use for pyritic copper ores, but since the introduction of pyritic smelting has been largely given up, and is avoided whenever possible.

At Rio Tinto, however, heap-roasting is still carried out on a scale of great magnitude, not, however, to prepare the ore for smelting, but to oxidize the copper sulphide to sulphate, in order that it may be leached out from the heaps *in situ.*

Heap-roasting may also be sometimes necessary during the early stages of smelting at a newly-opened mine, and when the blast-furnaces of an established smelter gain on the ordinary roasting plant.

It has the following disadvantages :—

1. The length of time required for the operation.
2. The irregularity of the oxidation.
3. The liability to losses by wind and rain.
4. The fumes are destructive to crops and vegetation, and are always a nuisance.
5. The waste of sulphur which might be utilized as fuel in the blast furnace.

Heap-roasting can only be employed where the SO_2 will not be a nuisance to the neighbourhood and where there is no vegetation which it can injure.

On the other hand, no expensive plant is required, and the product is in a suitable form for smelting in blast furnaces.

Size of Heap.—A good size for a heap for ordinary ore is about 40 by 24 feet and about 7 feet high above the bed of fuel. Contents about 250 tons. The height is important, and should be varied according to the percentage of sulphur in the ore. An ore with only 15 per cent. of sulphur may be piled to a height of 9 feet, whilst for solid pyrites containing 35 to 40 per cent. sulphur the height should not exceed 6 to 8 feet.

The time required for burning will be on the average about 75 or 80 days, much, however, depends on the nature of the ore and on the amount of sulphur which it is permissible to retain in it. The removal and rebuilding of the heap will occupy about ten days more.

Selection of Site.—The first point to consider is the prevailing direction of the wind. The fumes must not be blown towards the works, offices, or dwelling-houses. The site must be one protected, as far as possible, from violent winds. It should, too, be either perfectly dry or susceptible of thorough drainage. In any case, it should be drained to prevent loss of $CuSO_4$, if copper is present, when the heap is exposed to heavy rains.

If the roasting yard is on a slope there should be a deep trench along its upper side to catch any water which may run or drain down from the higher ground.

The site having been selected, the surface soil, old roots, etc., should be removed, and the space filled with broken stone, gravel, or coarse tailings, on the top of which should be put a layer of loam or clayey sand. This should be well beaten down, perfectly flat, so that it may be impervious, but should be slightly inclined.

Open drains leading to a sump containing scrap iron should be constructed between the heaps to receive any solution of $CuSO_4$ which may drain from them in wet weather.

In making the pile there should be first placed upon the bed a layer of fine ore to the depth of about 4 or 6 inches. This will prevent the calcined ore from sticking to the bed, and in time will gradually become calcined itself when it should be removed and fresh fines substituted.

Upon this the fuel, which may be wood of any kind, is laid to a depth of from 8 to 14 inches, according to the nature of the ore. Brushwood and chips are intermingled with the larger pieces of wood to assist in their ignition. Transverse channels about 6 inches wide are made in the bed of fuel about 10 feet apart, and these communicate with three rudely-constructed chimneys leading through the top of the pile. The chimneys may be made of old boards, split logs, or old corrugated iron, worn-out jig screens, and the like, with coarse or lump ore around.

The main body of the heap is then made up of large lumps of ore, over which smaller lumps are piled. The external layer must consist entirely of fine ore.*

It is generally advisable to get the pile ignited as quickly as possible by leaving the top uncovered. But as soon as this is effected the top must be covered with fine ore, and as the burning proceeds, any broad fissures formed either in the top or sides must be filled up with fines. After ignition the pile is best left alone, except for the repair of fissures caused by irregular settling, and for this purpose it should be inspected daily.

Roasting in heaps at the Tyee smelter (British Columbia) was brought as near perfection as is possible with such a process. The ore, which contained Cu 4·56 per cent., Fe 12 per cent., S 16·6 per cent., and barytes 37·3 per cent., was brought to bins over fixed screens set at 40° and to $\frac{3}{8}$-inch size.

The fines passed to a compartment in the centre of each bin, and were briquetted. The over size was taken to the roasting piles, also the briquettes after drying.

The level of the roast yard was 8 feet below the tram tracks in front of the discharge gates of the bins. These tracks extended through the yard longitudinally on trestles, of which there were six 60 feet apart. At right angles there were six trenches, each 4 feet deep, and 35 to 40 feet apart, in which the cars for the removal of the roasted ore ran. These and the trestles divided the yard into beds (Fig. 1).*

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* For further details see Peters, *Modern Copper Smelting*, pp. 104, *et seq.*

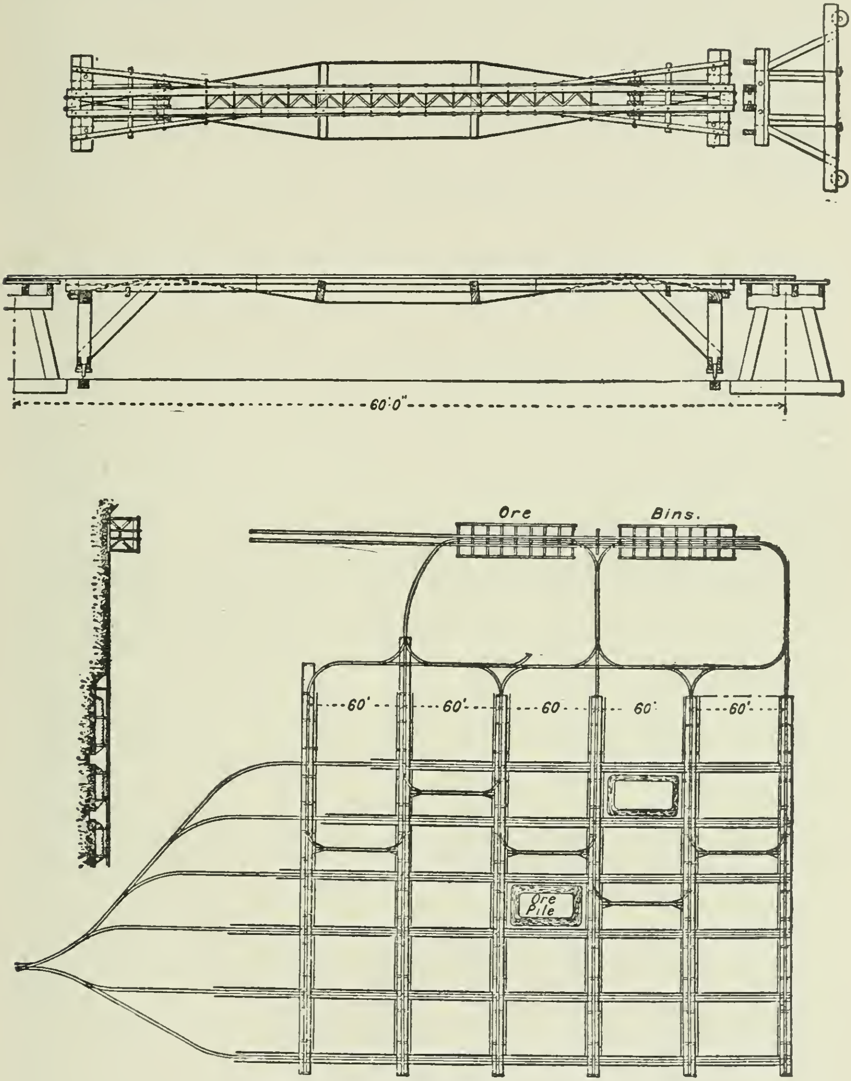

Fig. 1.—Arrangements of Roasting Heaps at the Tyee Smelter.

Between the permanent trestles there were movable bridges travelling on wheels, so that they could be moved over the ore beds as required. They carried tram tracks, which by means of adjustable curves allowed the cars to run over them from the trestles. The ore heaps or piles were 50 feet long, 24 feet wide, and 7 feet high, and each held 300 tons. They were not built higher in order to shorten the time of roasting and also the time of exposure to the heavy rains of the district. The ore was piled on a 12-inch layer of cord-wood, each pile requiring eight cords. The cars tipped from both sides, and no shovelling was required, except to level the pile when completed.

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* *Eng. and Min. Journ.*, Nov. 1904.

The time required for burning was three weeks, and the average amount of sulphur in the roasted ore was 7 per cent.

Stall-Roasting.—Roasting in stalls is only practised for ores suitable for heap-roasting. Stalls are small paved enclosures open at the front, the three other sides being permanent walls. They are usually built, back to back, in rows, with a flue, which terminates in a chimney stack, running between the rows. The side walls are pierced with small openings for the admission of air, and the back walls with similar openings communicating with the flue.

A good size of stall for ordinary ores is length 8 feet, breadth 8 feet, and height 6 feet, each of these will hold a charge of from 20 to 25 tons. They may be built of ordinary bricks, slag-bricks, or stone. Some are as large as 12 feet by 9 feet by 5 feet.

The stalls are charged as follows :—The wood and brushwood for kindling are first placed on the floor of the stall, the lumps in gradually decreasing size being piled upon it.

Some vertical pieces of wood are put in at the sides, and, as the stall is being filled, the front wall is built up with large lumps of ore. The top is covered with several layers of fine ore, the uppermost being sometimes of calcined fines ; the draught is thus directed to the openings in the back wall leading into the flue. In some cases, a sheet-iron cover is placed over the fines.

The heat must be carefully regulated by closing the external air openings, partially or wholly when necessary, and plastering up the front wall. If this be neglected, part of the charge will be sintered or fused, and imperfectly roasted.

The time required for roasting will usually be only about ten or twelve days, and in this respect stall-roasting has an advantage over heap-roasting. Other advantages are the carrying off of fumes by a chimney stack, the prevention of loss by wind and by leaching, and, as a rule, the roasting is more thorough.

Roasting in Kilns.—Kiln-roasting proper is confined to the treatment of pyrites rich in sulphur, often containing small amounts of copper, for the manufacture of sulphuric acid. The kilns, which are termed "pyrites burners," are small rectangular chambers about 4 feet 10 inches by 4 feet 10 inches by 4 feet, in which the pyrites is burned without carbonaceous fuel, this only being required to start the kiln.

The burnt pyrites is discharged more or less continuously through the grate at the bottom, and the gases are led to sulphuric acid chambers. The product is termed "burnt ore," and when cupriferous is sold to copper smelters.

Roasting of Ore Fines and Concentrate.—In these cases the ores are in a more or less pulverized condition. The furnaces employed are generally of the reverberatory type, but shaft furnaces and blast-roasting apparatus are also in extensive use. The reverberatory type will be first considered.

In order that the roasting may be efficient and effected without loss of time, it is necessary that as large a surface of the ore, as possible, should be continually exposed to the action of heat and air. Hence, the depth of the bed of ore in the furnace must be determined for each material, and the ore must be stirred or rabbled by hand or mechanically as continuously as possible. An ore is said to be roasted " dead " when all the sulphur which can be expelled by roasting has been driven off. In actual practice a small amount of sulphur will always remain in the roasted ore. " Dead " roasting is not often necessary, and sometimes a certain percentage of sulphur must be left unoxidized.

Furnaces of the reverberatory type may be divided into the following classes :—

I. Furnaces with fixed hearths—hand-rabbled.
II. ,, ,, —with mechanical rabbles or ploughs.
III. ,, revolving hearths.
IV. Muffle furnaces.

I. Furnaces with Fixed Hearths—Hand-Rabbled.—The old furnaces of this type with short beds, in which the charge was spread over the whole of the bed, and rabbled and raked out at the end of the roasting, are practically obsolete except for one or two special purposes.

They are very wasteful in fuel, difficult to work on account of the changes in temperature required, a low temperature being necessary at the beginning of the roast and a high temperature at the end, and are expensive in labour.

The best form of this kind of furnace is the hand-worked, long-bedded, four-hearth roaster, or calciner, as it is often called (Figs. 2 and 3).*

This furnace has been, and is universally successful as a roaster, as the ore can be rabbled more or less, as required, on any part of the bed, and when, as in some lead ores, accretions form on the bed they can at once be removed, a very difficult matter in a mechanically rabbled furnace. It has one disadvantage, and that is the high cost of labour required for working it, and this in many localities prohibits its use. It is a simple reverberatory furnace, the cooler parts of which are sometimes built of an ordinary red brick, except the hearths, which should be of hard burnt fire-bricks or tiles. Usually the bed consists of four hearths, each having a step of about 2 inches on the side towards the fire-bridge, so that the ore on one can be kept from mixing with that on the adjoining hearths. The dimensions of each hearth in the largest furnaces are 16 feet long by 16 feet wide, but they are sometimes only 12 by 12 feet. The number of hearths, and consequently the length of the furnace, depends on the amount of heat the ore will generate during roasting. This, of course, will vary with the percentage of sulphur the ore contains. Hence, in practice it is customary to have a four-hearth furnace for ores having 25 per cent. of sulphur or more, a three-hearth for ores with 20 per cent., a two-hearth for ores with 15 per cent., and so on ; but there can be no fixed rule, as the nature of the gangue and especially of the ore and of the associated minerals are important factors which must be considered. Thus, for example, iron pyrites will need a furnace one hearth longer than magnetic pyrites.

The dimensions of the fire-box should be not less than 8 feet by 2 feet

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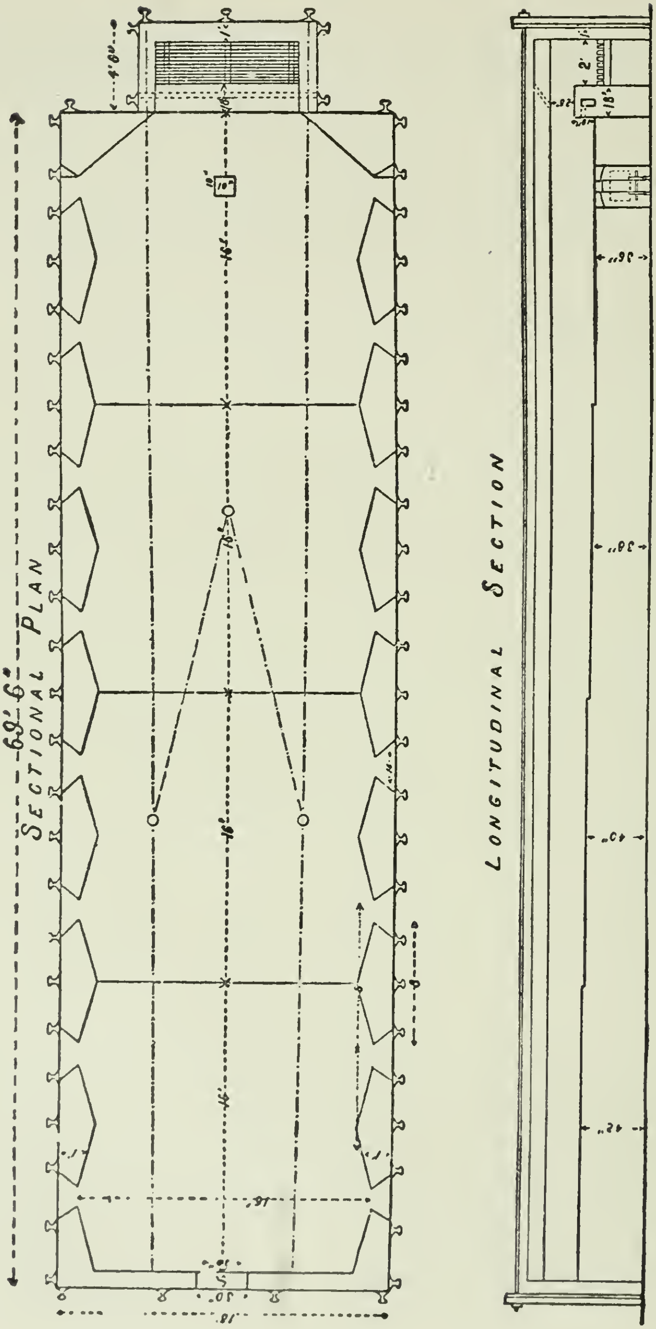
* Peters, *Modern Copper Smelting*, p. 175.


69' 6"
SECTIONAL PLAN
LONGITUDINAL SECTION
4' 6"
10"
16'
18'
14'
8'
18'
2'
18"
36"
40"
45"

Figs. 2 and 3.—Four-Hearth Roasting Furnace.

6 inches by 2 feet for a furnace with four 16-foot hearths; but here again there can be no rule, as they depend on the character of the fuel. The fire-bridge should be air-cooled, and have openings for the admission of air to the interior of the furnace.

There should be two working doors to each hearth on each side of the furnace. They should be closed by an easily removable iron plate.

In the hearth next the fire-bridge is an opening for the discharge of the roasted ore into a truck in the vault below. This is kept closed with a cast-iron plate during working.

In working the furnace the finished charge on the hearth next the fire-bridge is raked through the discharge opening into the truck below it, and the charge on the next hearth raked upon it by means of a rabble. The charges on the other hearths are similarly raked on to the neighbouring hearths. A charge of fresh ore is then dropped from a hopper upon the hearth furthest from the fire. In this way the ore, after having been well rabbled on each hearth, passes from the coolest to the hottest part of the furnace, and does not reach it until well oxidized and there is no danger of clotting. For ordinary ores the charge of a 64 feet by 16 feet furnace is about 2 tons, and as a charge is drawn about every four hours the output will range from 12 to 16 tons roasted down to about 6 per cent. of sulphur per twenty-four hours.

In roasting lead ore at some works, the hearth next the fire-bridge is at a lower level than the others, and is heated to a high temperature to sinter the ore and obtain a product more suitable for smelting in the blast furnace than ore which has been merely roasted; but much silver and lead is lost by volatilization when this procedure is followed.

The shelf burner, a hand-rabbled furnace once largely used in zinc works, is described on p. 469.

II. **Furnaces with Fixed Hearths** in which the ore is stirred and raked by means of rabbles or rakes worked by machinery.

The most important furnaces of this class are:—

The Brown Horse-Shoe and Straight Line.
,, Wethey.
,, Ropp.
The Edwards.
,, Merton.
,, Pearce Turret.
,, MacDougall and its modifications.

For others used, especially in roasting zinc blende, see pp. 471-479.

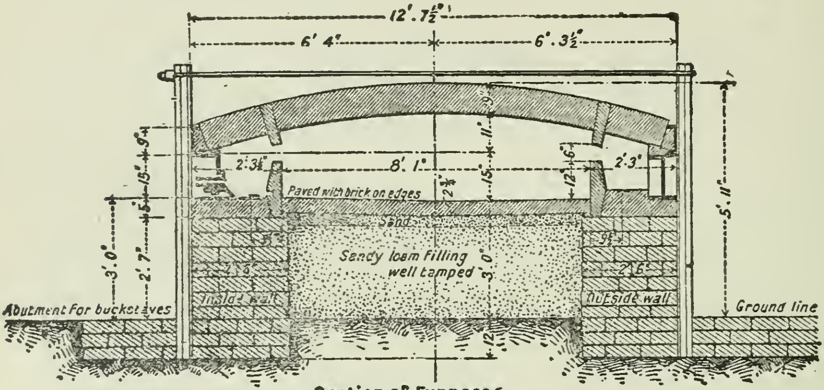
The Brown Furnace.—This furnace was originally built in a horse-shoe form, and is known as the "horse-shoe" furnace. It is in extensive use in the United States.

It is now sometimes built in a straight line. A transverse section is shown in Figs. 4 and 5. In its most improved form as a straight-line furnace the rabbles after passing through the furnace are carried on rails over the top of the arch or under the bed to cool, and then pass again into the interior of the furnace.

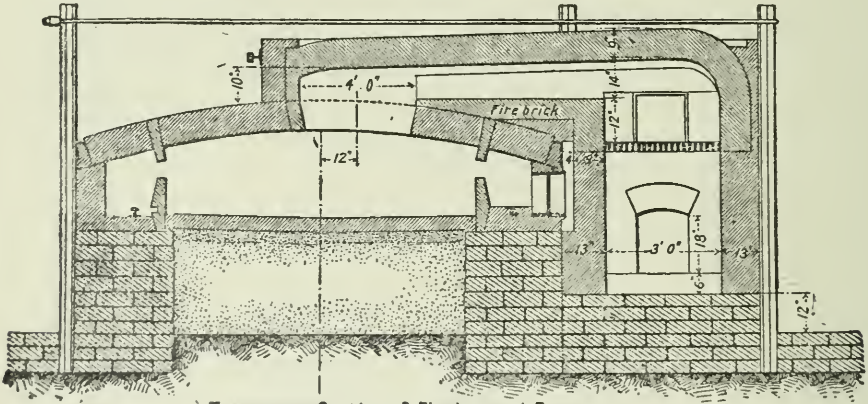
At each side of the hearth is a narrow chamber separated from it by fire-tiles projecting downwards from the roof and upwards from the hearth, having a narrow longitudinal slot between them.

The rabble arms carrying the stirring ploughs or rakes are supported at the ends by small carriages. The carriages are drawn by an endless steel rope, and run in one chamber on a rail, and in the other on a flat track.

The straight furnace ranges from 60 to 180 feet in length, is 10 feet wide, and is used where space is limited, otherwise the horse-shoe or elliptical type is sometimes preferred. There are usually four stirrers, but in the smallest furnaces only two; and two, three, or four fire-boxes, according to the size of the furnace. Gas firing is also employed.


12'.7½"
6' 4"
6'.3½"
9"
11"
15"
2'.3½"
8'. 1"
2½
15"
12½
6½
2'.3"
5'. 11"
3'.0"
2'.7"
Paved with brick on edges
Sand
Sandy loam Filling well tamped
3'.0"
Inside wall
Outside wall
2'.6"
Abutment for buckstaves
Ground line
12"

Section of Furnace


10"
4'.0"
14"
Fire brick
12"
12"
13"
3'.0"
18"
13"
6"
12"

Transverse Section of Firebox and Furnace.

Figs. 4 and 5.—Brown Furnace.*

In the horse-shoe type a furnace in which the roasting part of the hearth is 180 by 8 feet will have 78 by 8 feet of hearth for cooling the roasted ore and the rabbles.

The furnaces are closed at each end of the hearth by sheet-iron flap-doors, which are lifted automatically as the rabble arms pass in and out.

At the Edgar Zinc Company's works near St. Louis, a horse-shoe furnace 55 feet in diameter, with a roasting area 135 feet long and 8 feet wide and four fire-boxes, roasted 11 to $12\frac{1}{2}$ tons of ore containing 30 per cent. of sulphur down to 0·5-0·7 per cent. in twenty-four hours.*

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* Collins, *Lead*, p. 91.

The Wethey Furnace.—This furnace, which is shown in section in Fig. 6, is similar to the Brown straight-line furnace, but it has two superposed hearths, the upper for roasting, the lower for cooling, and the rabbles are of different construction.

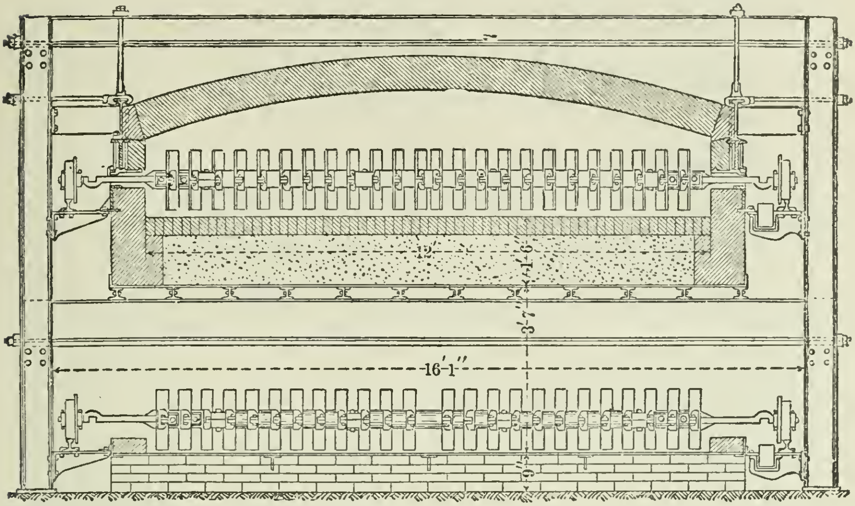
12'
1'-6
3'-7''
16'-1''
9''

Fig. 6.—Wethey Furnace—Section.†

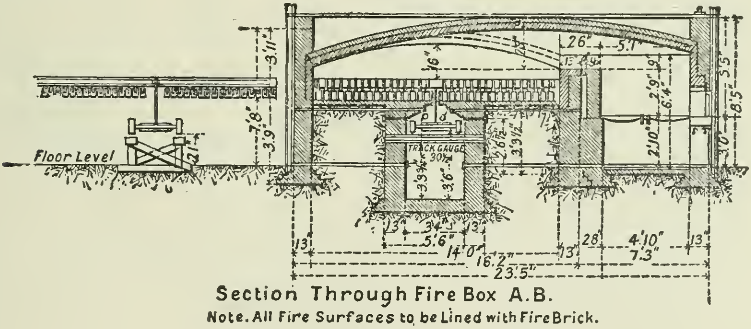
Floor Level
3'11"
7'8"
3'9"
21"
16"
26"
5'1"
13"
4"
9"
2'9"
6'4"
5'5"
8'5"
2'10"
3'0"
p
d
TRACK GAUGE 30½
3'9½"
3'6"
2'6½"
3'3½"
13"
3'4"
13"
5'6"
13"
14'0"
16'2"
13"
28"
4'10"
13"
7'3"
23'5"
Section Through Fire Box A.B.
Note. All Fire Surfaces to be Lined with Fire Brick.

Fig. 7.—Ropp Straight-line Furnace.‡

Each hearth is 120 feet long by 12 feet broad, the upper hearth being heated by four fire-boxes.

A special feature of this furnace is the manner in which the upper arch is supported. The skewbacks are I beams held in place by I-beam buck-

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* Ingalls, *The Metallurgy of Zinc and Cadmium*, p. 96.

† Ingalls, *Zinc and Cadmium*, p. 112.

‡ Collins, *Lead*, pp. 100 and 101.

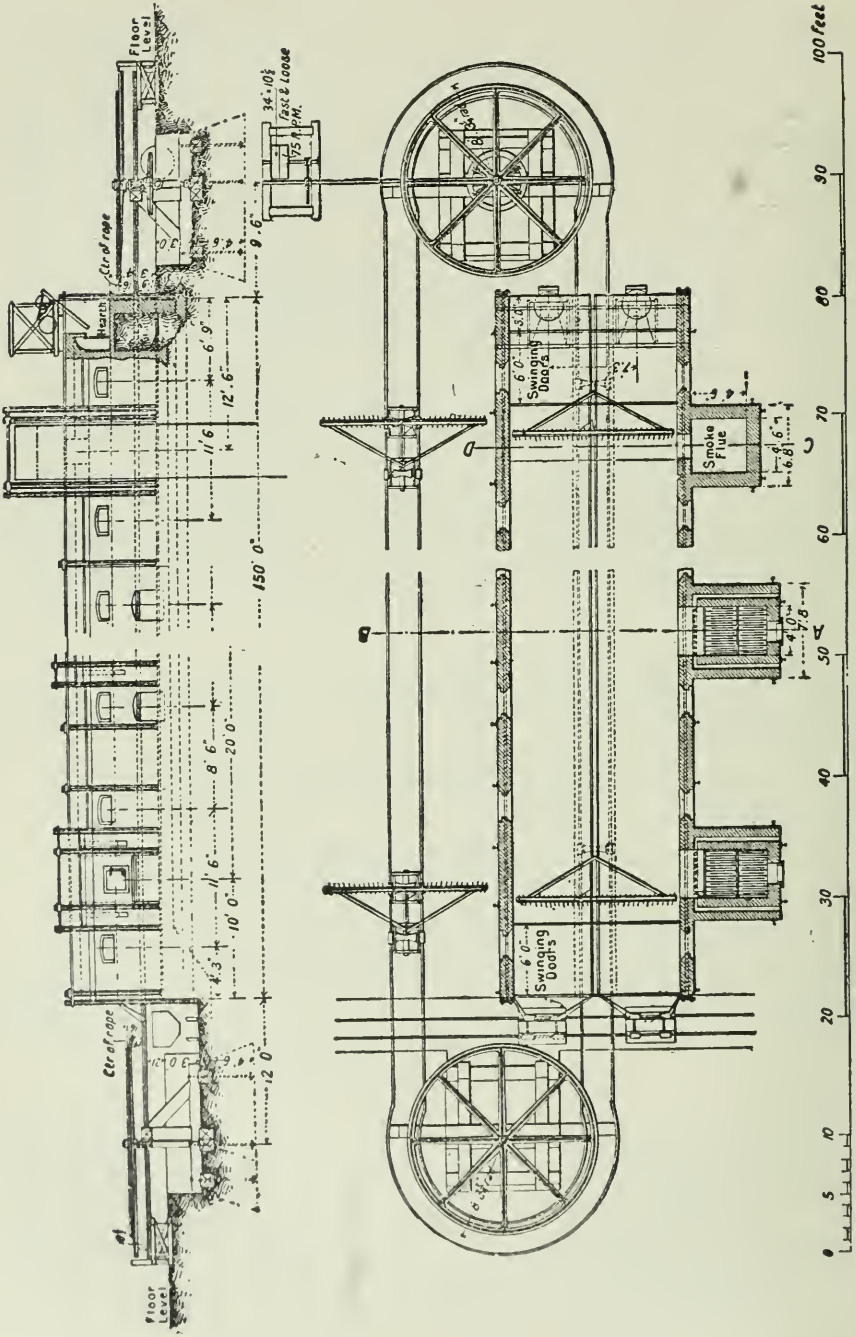
Floor Level
Ctr of rope
Hearth
34"×10½"
fast & loose
75 R.P.M.
9'6"
6'9"
12'6"
11'6"
150'0"
8'6"
20'0"
11'6"
10'0"
4'3"
12'0"
3'0"
Swinging Doors
6'0"
Smoke Flue
6'6"
6'8"
4'0"
7'8"
0
5
10
20
30
40
50
60
70
80
90
100 feet

Fig. 8.—Ropp Straight-line Furnace. (Collins, *Lead*, pp. 100 and 101.)

stays. It is, hence, possible to have a slit running the entire length of each side of the hearth. Through this slit the ends of the rabble arms pass, and are fitted to small carriages which run outside the furnace, and are thus not exposed to the heat inside. The rabble arms, which are two in number, are hauled by endless chains. They move the ore along the roasting hearth, from the end of which it falls upon the cooling hearth, and is then moved by them to the discharge end. At some works the cooling of the roasted ore is hastened by cold-water pipes laid in the floor of the lower hearth.

The blades in alternate rabbles are set at opposite angles, so that the ore is not forced towards only one side of the hearths.

The Ropp Straight-Line Furnace is a long reverberatory resembling the Brown straight-line furnace, but different from it in the method of supporting the bar carrying the stirring ploughs, and of protecting the supporting carriages from the heat (Figs. 7 and 8). In the middle of the hearth is a longitudinal cast-iron slot extending from one end to the other. Below it is a chamber containing the track upon which the carriage supporting the arms runs. A vertical arm passing through the slot connects the bar, carrying the rabbles, with the carriage below. There are four sets of rabbles, each fitted to its own carriage, and the carriages are attached at equal distances from each other to a steel wire rope by which they are hauled. The track is continued outside the furnace and parallel to it except for the curve at each end. The driving rope passes around two large sheaves at the furnace ends, so that the rabbles, after passing through the furnace, are drawn along the track outside, and thus are thoroughly cooled.

The dimensions of the hearth of a standard furnace are:—Length 105 feet, breadth 11 feet. There are three fire-boxes and four sets of rabbles to each furnace. Each rabbling arm makes a complete revolution in 3 minutes. Larger furnaces are also in use, the largest having a hearth 150 by 14 feet.

At the Selby Smelting Works, Cal., a furnace of the standard size had an output of 25 to 35 tons of lead ore roasted down to 4 to 5 per cent. sulphur in twenty-four hours, the raw ore containing 20 to 25 per cent.*

The Edwards Furnace.—This furnace is made with either a tilting or a stationary hearth (Figs. 9, 10, 11).† The former is a single-hearth reverberatory furnace, with mechanical stirrers, enclosed in a casing of boiler plate. In the tilting furnace the sides are made of two girders, each 63 feet long, built on the cantilever principle. The bed is 6 feet 5 inches wide. The whole is supported about 2 feet clear of the ground upon a couple of pivots placed midway between the ends, and is held at the desired inclination by a couple of screw-jacks. The rabbling is done by a line of 15 revolving stirrers attached to vertical stems, which pass through the arch of the furnace. The stirrers consist of five removable ploughs fitted to a cast-iron arm, which describes a horizontal circle in the ore. Each stirrer revolves in the opposite direction to its immediate neighbour, and the ore is thus made to travel in a zig-zag course along the bed of the furnace.

The five rabbles nearest to the fire-box are hollow, and are cooled by a stream of water, which passes down a central pipe in each, and after ascending escapes into a channel which encircles the rabble stem on the top of the arch.

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* Collins, *Lead*, p. 37.

† *Mining and Scientific Press*, July, 1910.

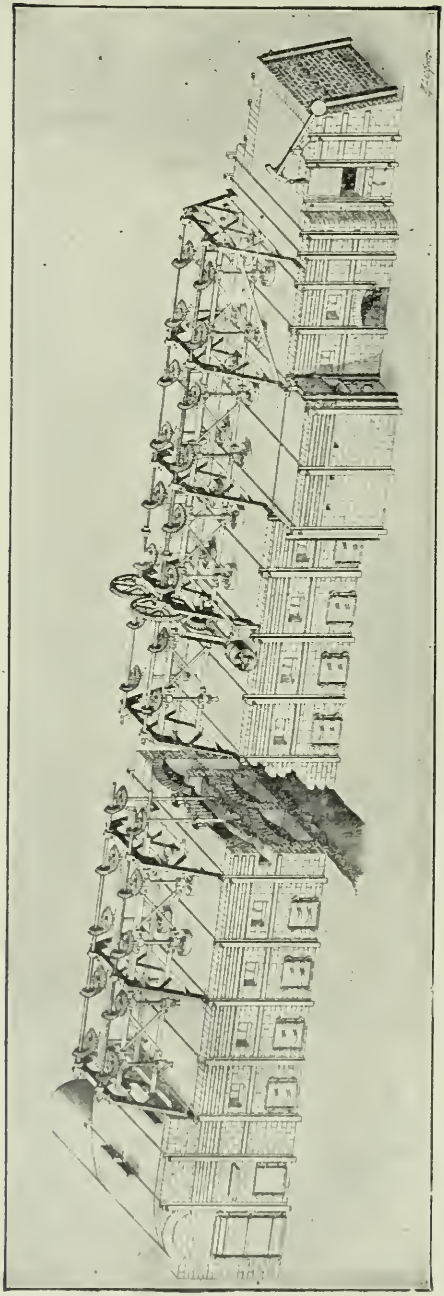
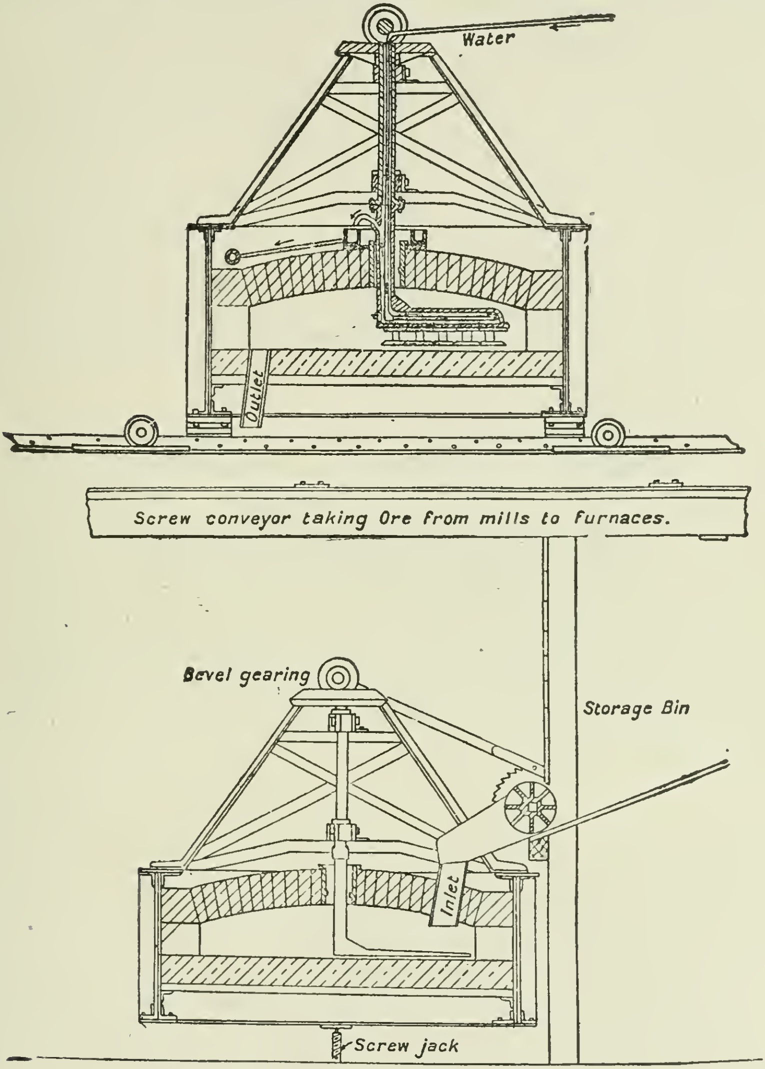


Fig. 9.—Edwards Furnace (Fraser and Chalmers)

At the Boulder Main Reef Company's works, W. Australia, the inclination of the furnaces was about 9 inches in the total length. The layer of ore on the hearth was usually 2 to 3 inches deep, and two hours were occupied in its journey from the inlet to the discharge.


Water
Outlet
Screw conveyor taking Ore from mills to furnaces.
Bevel gearing
Storage Bin
Inlet
Screw jack

Figs. 10 and 11.—Edwards Furnace—Sections.*

When roasting heavy auriferous concentrate sweet, this furnace has a capacity of 7 to 9 tons per twenty-four hours, but when roasting ore carrying 6 per cent. of sulphur sweet, it has a capacity of 21 tons. The Edwards furnace with stationary hearth is built at a slight inclination, if necessary, sloping toward a discharge end (Fig. 9). The amount of inclination for a given ore should first be determined.

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* *Trans. Inst. Min. and Met.*, vol. xiii., p. 29.

The furnace is built of brick, and stayed like an ordinary reverberatory. The stirrers are of the same type as in the tilting furnace, but the gear for driving them, instead of being above the furnace, is sometimes placed in a tunnel beneath the hearth.

The furnace bed is usually 9 feet wide, but may be made up to 14 feet. The length may be 100 feet or more, according to the nature and amount of the material to be treated. In addition to the end fire-place there may be two or more at the sides.

One of these furnaces with a hearth 120 feet by 9 feet wide will roast 60 tons of W. Australian ore containing 6 per cent. of sulphur in twenty-four hours, so that it will be suitable for treatment by the cyanide process.

In some of these furnaces there are two lines of rabbles instead of a single line. They are called "duplex" furnaces, and many of the newer furnaces are of this type.

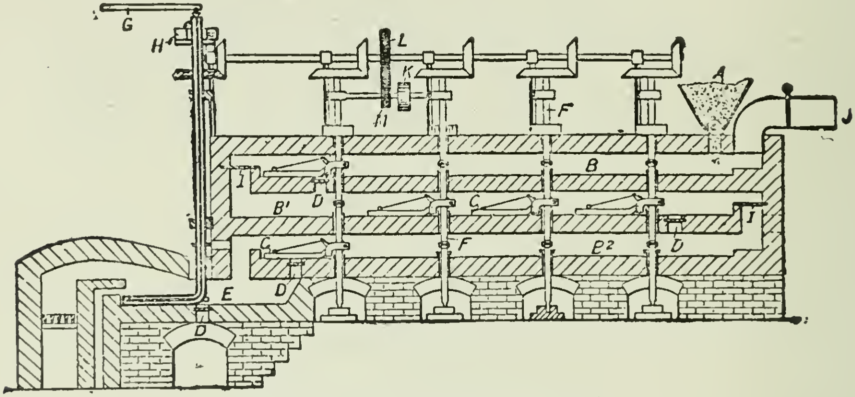

Fig. 12.—Merton Roasting Furnace.*

The Merton Furnace (Fig. 12).—This furnace resembles the Edwards furnace in having revolving rabbles, but differs from it in having three superposed hearths and a special finishing hearth. The hearths are level, and communicate with one another by vertical channels.

The rabbles, of which there are five on each arm, are precisely similar to those of the Edwards furnace, but the stems to which the arms are attached pass through all three hearths, and are supported in sockets below the lowest hearth. There are four sets of rabbles for the main hearths, and one or sometimes two water-cooled rabbles for the finishing hearth.

The ore is fed in at the coolest part of the uppermost hearth, is gradually traversed by means of the rabbles along each hearth, and finally discharged through an opening in the finishing hearth into a truck below it.

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* *Eng. and Min. Journ.*, Nov. 1903.

In S. Wales several Merton furnaces have been erected for roasting zinc blende. One of these has four hearths 10 feet wide, with four sets of rabbles. The finishing hearth is 6 feet wider than the others, and has two rabbles cooled by circulating water in the usual way. The capacity of a furnace with three hearths 22 feet long by 6 feet 6 inches wide is 18 to 25 tons of West Australian ore in twenty-four hours. When working on zinc ore containing Zn 33 per cent., Pb 19 per cent., and S 20 per cent., about 8 tons are roasted down to 1·5 per cent. S per day.*

Compared with the Edwards furnace, the Merton has the advantages of occupying less floor space and consuming less fuel, it is also said to give a better roast, but produces more dust.

Both the Edwards and the Merton furnaces are in extensive use at Kalgoorlie. There are about 100 at work roasting ore for the cyanide process, and of these more than half are of the Edwards type.

The Pearce Turret Furnace.—This consists of a reverberatory hearth built in a circular form. The inner vertical wall is provided with a continuous slot, and to allow of this that side of the arch is supported by stirrups from I beams arranged radially over the top of the furnace. The furnace is shown in section in Fig. 13.

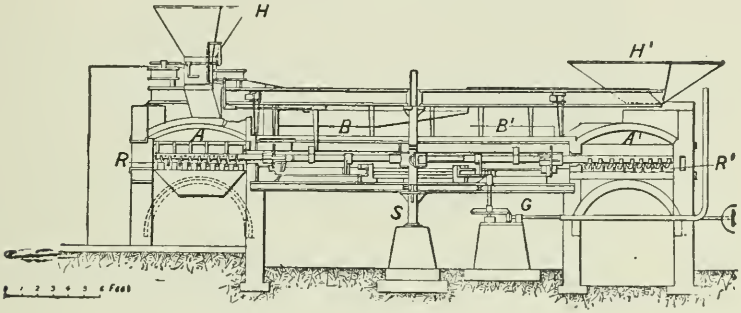

Fig. 13.—Pearce Turret Furnace.†

In the open space within the circle a vertical shaft, revolved by gearing, carries four horizontal radial arms of 5-inch pipe, to which are attached rabble-blades for stirring the ore. Generally only two of the arms carry rabbles, and for some pyritic ores there is only a single arm which stops automatically for a short time in the space above the discharge opening. The arms carrying the rabbles pass through the slot, and as they are revolved the slot is closed by a band of sheet steel carried by the frame on which the rabbles are suspended. Air is forced through the arms, and is discharged against the rabble-blades, thus cooling the ironwork and furnishing heated air for the oxidation of the ore. The air is cut off automatically where the ore is charged in, and is only admitted after the roasting has begun. The hearth is heated by two, or sometimes three, step-grate fire-places. Oil firing is also employed. The ore is fed in automatically through a hopper, is pushed along the hearth by the rabbles, and discharged automatically into trucks underneath. The furnace is built in three sizes—viz., 36 feet in outside diameter with a hearth 6 feet wide, 40 feet diameter with an 8-foot hearth, and an intermediate size. When working on pyritic ores containing about 40 per cent. sulphur the capacity of a 36-foot furnace is about 15 to 20 tons roasted down to 6 or 7 per cent. sulphur in twenty-four hours. The Pearce furnace is also made with two or more superposed hearths.

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* Danvers Power, *Eng. and Min. Journ.*, Nov. 1903.

† Roberts-Austen, *Introduction to Metallurgy*, p. 349.

The MacDougall Furnace.—There are three chief modifications of this form of furnace:—The Evans-Klepetko, the Herreshoff, and the Wedge.

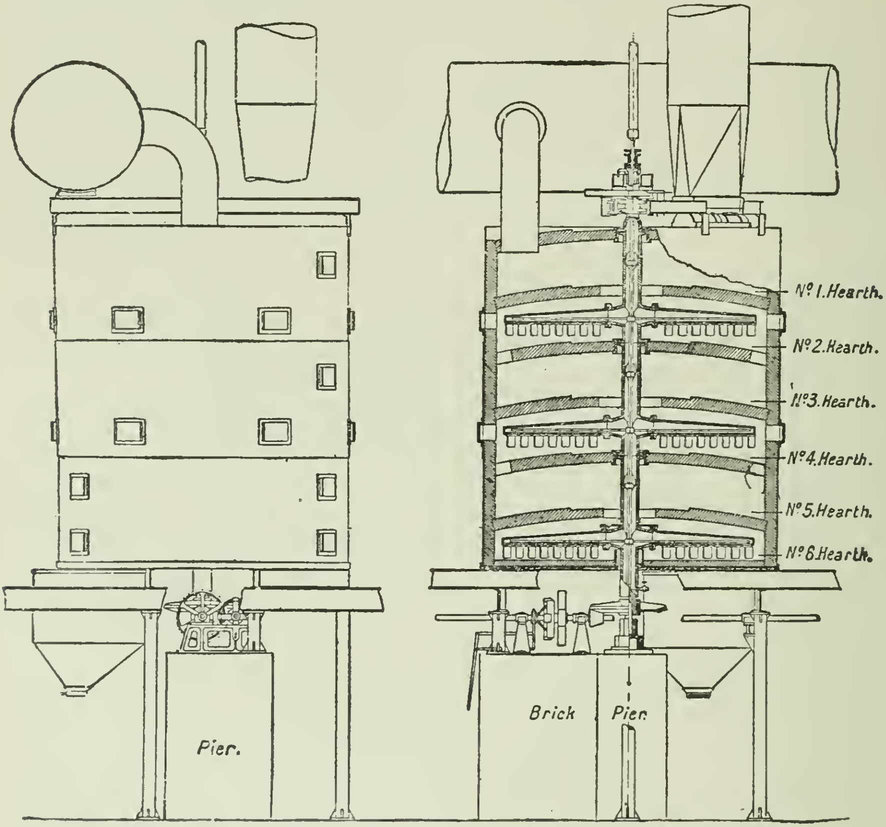

Fig. 14.—MacDougall Roasting Furnace (Evans-Klepetko Modification).

It is the most important type of roaster, especially for copper ores, on account of its efficiency and low working costs.

The Evans-Klepetko is the furnace employed at the Washoe and Great Falls Works of the Anaconda Company, and at many other important smelters. It consists of a cylindrical vertical shell of $\frac{3}{8}$-inch steel, lined with 8 or 9-inch bricks, with six hearths provided with openings alternately at the centre and periphery, through which the ore is rabbled from hearth to hearth, and finally discharged (Fig. 14). A vertical hollow shaft, to which the six arms, which are also hollow, carrying the ploughs are attached, passes through the centre of the furnace. The ploughs are so set that they stir and push the ore toward the opening near the middle of the first hearth to the six openings at the periphery of the next, and so on alternately to the bottom, where the ore falls through a hopper into a truck or a bin below. The shaft and arms are cooled by water circulating through them. The air for the oxidation of the ore is admitted through the doors in the side of the furnace. The hearths, which are 30 inches apart, are arched and are levelled with coarsely crushed limestone.

The material to be roasted is either concentrate, which passes ¼-inch mesh, together with the very fine product from vanners, etc., or ore-fines of ½ inch size or less. It is fed continuously upon the uppermost hearth from a hopper by means of an automatic feed.

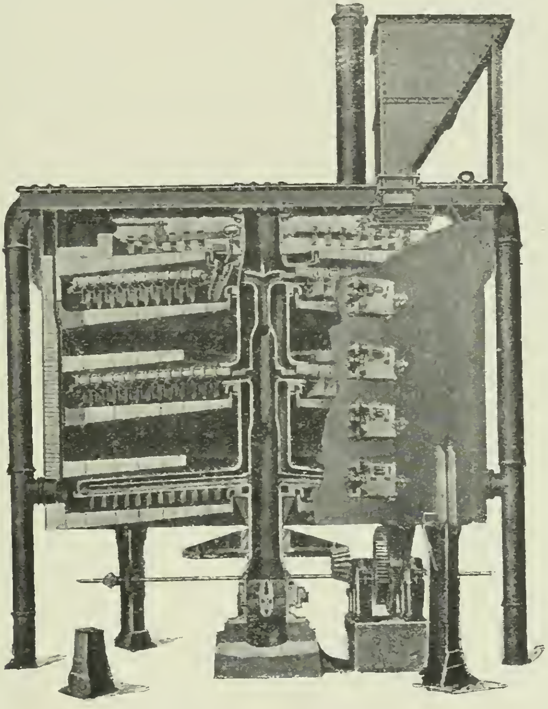

Fig. 15.—Herreshoff Furnace.*

If the ore is rich in sulphur it will burn of its own accord, but if poor, say below about 28 per cent., an external fire-place will be required. In the former case the furnace only requires to be heated on starting. The furnaces at Washoe, where there were 64 in 1911, are 16 feet in diameter, and are supported on a steel framework about 12 feet above the ground. Each furnace usually requires about 1·7 H.P. Under normal conditions each furnace will roast about 40 tons of an ore containing 38 per cent. of sulphur down to 6 per cent. in twenty-four hours.

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* Levy, *Modern Copper Smelting*, p. 74.

At the works of the Steptoe Valley Smelting and Mining Company, Nevada, there were 16 18-foot, six-deck furnaces with water-cooled shaft and arms, roasting 50 tons of concentrate of an average percentage composition of Cu 13·1, SiO_2 28·2, Fe 25·3, Al_2O_3 3·8, S 27·2, down to 8 per cent. of sulphur in twenty-four hours. The output was increased to 100 tons per furnace, by making the following alterations:—Water-cooling was given up and cooling by air, forced in at $2\frac{1}{2}$ inches pressure, substituted, some being blown upon the charge to promote oxidation. Oil firing was adopted, and, lastly, the uppermost hearth was built of cast iron.*

The Herreshoff Furnace, Fig. 15.—In this modification of the MacDougall furnace the central hollow shaft, 42 inches diameter, which carries the rabble arms, is in three sections, connected by tongue and groove joints, the bolt heads and nuts being protected from the heat by pockets filled with refractory material. Inside this shaft is a steel tube 18 inches diameter, to which pipes are fitted for supplying air for cooling the rabble arms. The air for cooling is forced into the tube at a pressure of 1·75 ozs.

Eight of these furnaces, 21 feet 7 inches in external diameter, each having six hearths for roasting and one for drying, have been erected at the works of the Arizona Copper Company at Clifton.

Sixteen have been used at the Edgewater plant, New Jersey, of the General Chemical Company, for roasting Spanish pyrites for the production of SO_2 for the manufacture of sulphuric acid.†

The Wedge Furnace, Fig. 16.—The chief feature of this furnace in which it differs from the preceding modifications of the MacDougall furnace, is the wide, accessible central shaft, 4 or 5 feet in diameter. This shaft is of $\frac{1}{2}$-inch steel plate protected from the heat by a lining of firebrick, and is said never to be too hot for a workman to enter to unbolt a rabble arm and refix a new one. The hearths are level, 16 inches apart; they are built of special bricks, and are each provided with two rabble arms carrying adjustable blades.

The shaft, to which the rabble arms are attached, is supported by a strong frame, which revolves on rollers supported by pedestals. It is revolved by means of bevel and worm gearing. On the top of the shaft is a water pan for supplying the water for cooling the rabble arms. The rabble arms can, if necessary, be cooled with air forced in under pressure.

The furnace itself stands on structural steel columns about 5 feet 9 inches high, to allow the discharge of the roasted ore to be received in cars.

The furnace is built in several sizes from 12 feet to 22 feet 6 inches in diameter, and with from three to seven hearths and a dryer-hearth. One has been constructed 32 feet in diameter, with only one hearth, for chloridizing-roasting. The ore is fed at the periphery of the dryer-hearth, and is rabbled to an opening at its centre, through which it falls upon the first roasting hearth in a dry and heated condition.

An external fire-place can be fitted if the ore is poor in sulphur.

The capacity of a furnace 20 feet in diameter roasting pyritic copper ores for matte smelting is said to be from 70 to 80 tons in twenty-four hours.

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* *Eng. and Min. Journ.*, June, 1913.

† *Min. and Scientific Press*, Nov. 1913.

Wedge furnaces have been installed in the copper department of the El Paso Works, Texas, in the lead smelting works at Trail, B.C., and in a modified form for roasting zinc blende at Anaconda.

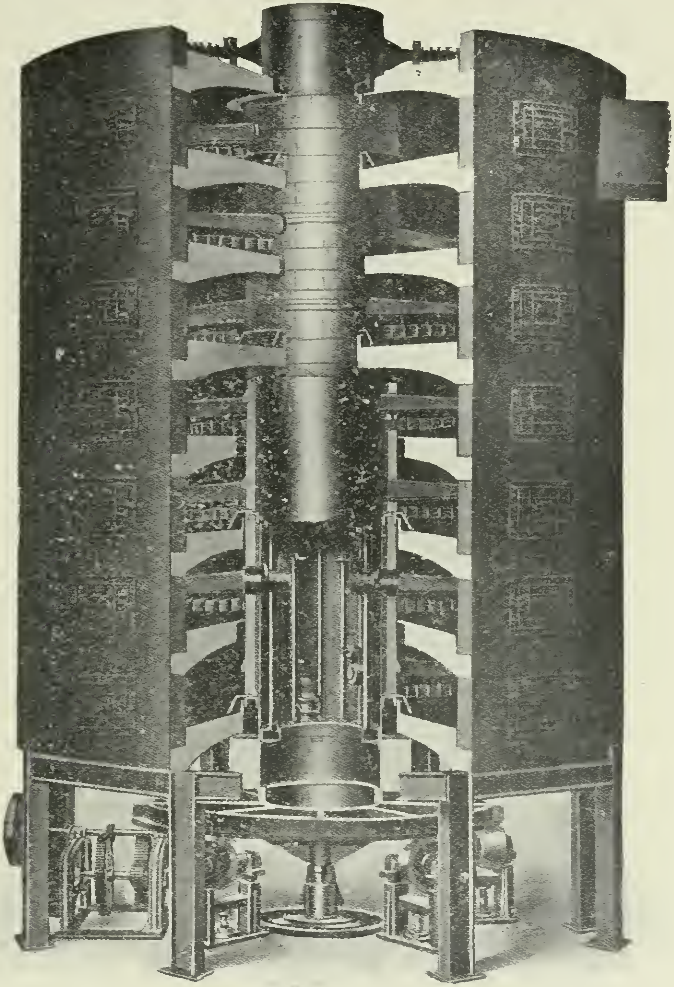

Fig. 16.—Wedge Furnace.

III. **Furnaces with Revolving Hearths.**—There are three classes of these furnaces :—

(*a*) Furnaces with revolving circular horizontal hearths and fixed rabbles.

(*b*) Revolving cylindrical furnaces with horizontal axes and intermittent discharge.

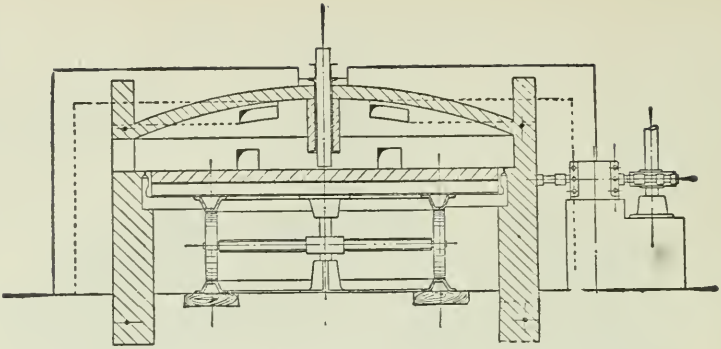

Fig. 17.—Revolving Hearth Furnace (Heberlein Type)—Section.

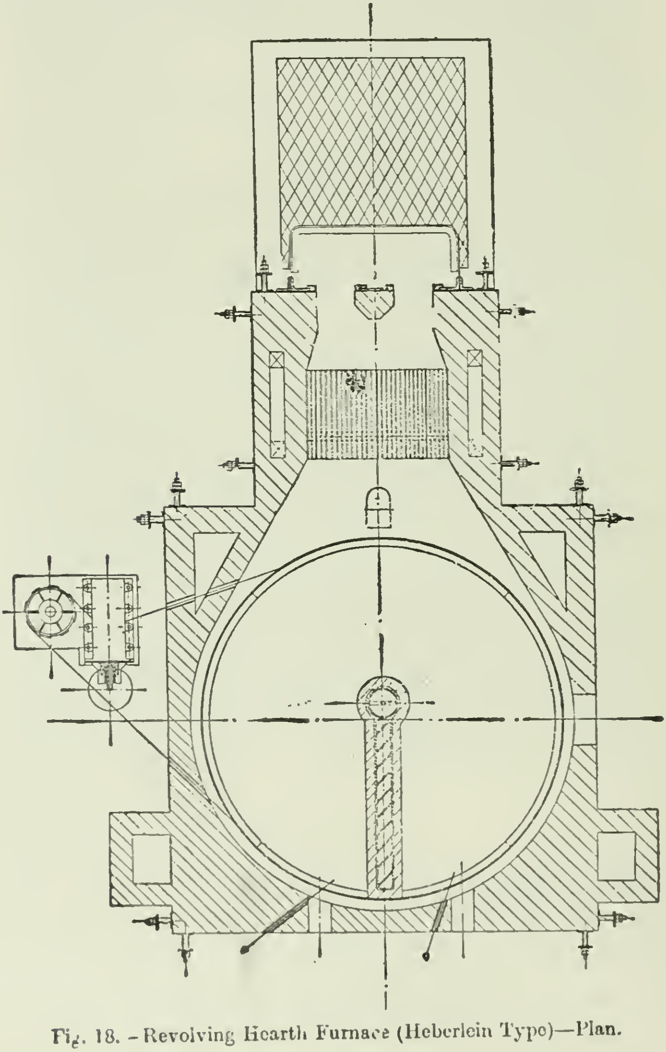

Fig. 18. – Revolving Hearth Furnace (Heberlein Type)—Plan.

(c) Revolving cylindrical furnaces with inclined axes and continuous discharge.

Furnaces with Revolving Circular Horizontal Hearths and Fixed Rabbles.—One of the oldest types is the *Brunton calciner*, which still survives in some tin and arsenic works in Cornwall (see p. 587). The modern modifications are the *Heberlein* and the *Godfrey furnaces*, which are chiefly employed in the partial roasting of ores before treatment by blast-roasting. The former consists of a flat circular hearth 26 feet in diameter supported on an iron frame, revolving on heavy wheels on a circular track, and driven by gearing. It has one rabble arm which is fixed, and an external fire-place * (Figs. 17 and 18).

The Godfrey furnace has an annular revolving hearth supported by cast-iron cantilevers fixed to a central column. The bottom of the hearth is built of cast-iron plates, upon which 2-inch fire-tiles are laid. The whole is carried on ball-bearings. There is one fixed arm with rabble-blades.†

Revolving Cylindrical Furnaces with Horizontal Axes and Intermittent Discharge.—The revolving cylindrical furnaces of this and the following class are modifications of the reverberatory furnace type in which the ore is turned over by the revolution of the furnace itself.

The Brückner Cylinder (Fig. 19), which was formerly perhaps in more extensive use than any other roaster, has during recent years been very largely displaced by the MacDougall and other mechanically rabbled furnaces. It consists of a cylinder of boiler plates lined with fire-bricks, which revolves on two iron rings resting upon four chilled-iron friction rollers or carrying wheels. The cylinder is revolved slowly, about one or two revolutions an hour, by means of a shaft driven by worm-gearing, and connected with two of the friction wheels. It has four openings for feeding and discharging and an opening at each end, one to the fire-box and one to the flue.

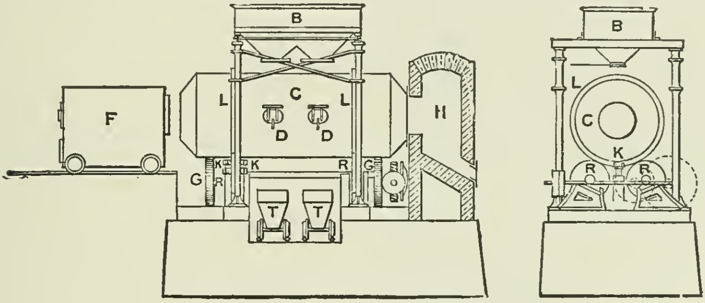

Fig. 19.—Brückner Cylinder.‡

The fire-box is sometimes mounted on wheels, which run on a track in front of the row of furnaces. It can thus be run in front of a cylinder which contains a fresh charge of pyrites, and when this has been heated sufficiently until the sulphur begins to burn, it can be moved to another cylinder to heat up its charge. To complete the roasting in the first cylinder it is brought back and again attached. As much dust is produced the cylinders must be connected with dust chambers. A standard size is 18 feet 6 inches by 8 feet 6 inches, but some have been made as large as 26 feet 6 inches by 8 feet 6 inches.

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* Collins, *Lead*, p. 99.

† *Trans. Inst. Min. and Met.*, vol. vii., p. 323, *et seq.*

‡ Roberts-Austen, *op. cit.*, p. 347.

The output of each furnace at Anaconda, when Brückner cylinders were in use there, was 12 tons per day of an ore containing 36 per cent. of sulphur roasted down to 8 per cent.

Any kind of ores can be treated, but when they contain large amounts of lead and sulphur, the treatment is difficult and requires great care, as they tend to fuse and form accretions or to ball, and the roasting is imperfect. When they contain little sulphur, as in the case of some silver ores which have to be chloridized, the fire-box has to be permanently attached. When the roasting is finished, the four openings are opened, the revolutions increased, and the ore discharged into a pit below.

The advantages of the Brückner cylinder are that the roasting is under the full control of the workmen, the ore can be kept in until it has been tested, the furnace is simple to work and not liable to get out of order.

Its disadvantages are that the work is intermittent, the fuel consumption rather high, and the rolling motion tends to ball the ore.

Revolving Cylindrical Furnaces with Inclined Axes and Continuous Discharge.—The three chief forms of this type of furnace are :—

(*a*) The White.
(*b*) The White-Howell.
(*c*) The Argall.

They are all improved forms of the old Oxland calciner which is still in use in Cornwall and in Sardinia.

The White Furnace is a long cylinder of boiler plate lined with fire-brick and inclined towards the fire-box end.

Four longitudinal ridges of brickwork project a little from the lining and lift the ore until it falls back in a thin stream through the flame from the fire-place and is discharged continuously at the fire-box end of the cylinder.

The cylinder is encircled by four or five cast-iron or steel rings, which rest on friction wheels, and is slowly revolved by gearing. The upper end of the cylinder is connected with a dust chamber.

The crushed ore is fed in continuously at the upper end, best through a shoot which delivers it at as low a height as possible into the cylinder, and passes gradually to the fire-box end, where it is discharged continuously into a chamber below. The amount of ore roasted depends on the percentage of sulphur it contains and of that which can be left in the product ; and the time during which it must be retained in the furnace is regulated by the speed at which the cylinder revolves and its angle of inclination. The cylinder is made of various sizes ranging from about 30 feet in length and 4 feet 6 inches in internal diameter to 60 or 80 feet in length and 7 feet in diameter. In South Wales furnaces of the latter size were employed in roasting "white metal," containing 76 per cent. of copper, down to from 1 to 3 per cent. of sulphur. They made eight revolutions per hour, and roasted 10 tons in twenty-four hours.

The furnace was chiefly used for the chloridizing-roasting of silver ores. If the ores, however, contain much sulphur it has the serious disadvantage that the salt has to be mixed with the ore before charging, whilst this is not advisable until after the greater part of the sulphur has been expelled. For chloridizing silver ores the furnaces were usually of small size, about 27 feet by 5 feet, and the revolutions 15 to 30 per hour. The output of such a furnace, working on a silver ore low in sulphur, would be about 30 or more tons of chloridized ore in twenty-four hours. The advantages claimed for this type of furnace as compared with the Brückner are :—

It is continuous in its operation.

The ore is automatically submitted to a gradually increasing temperature, and the consumption of fuel is lower.

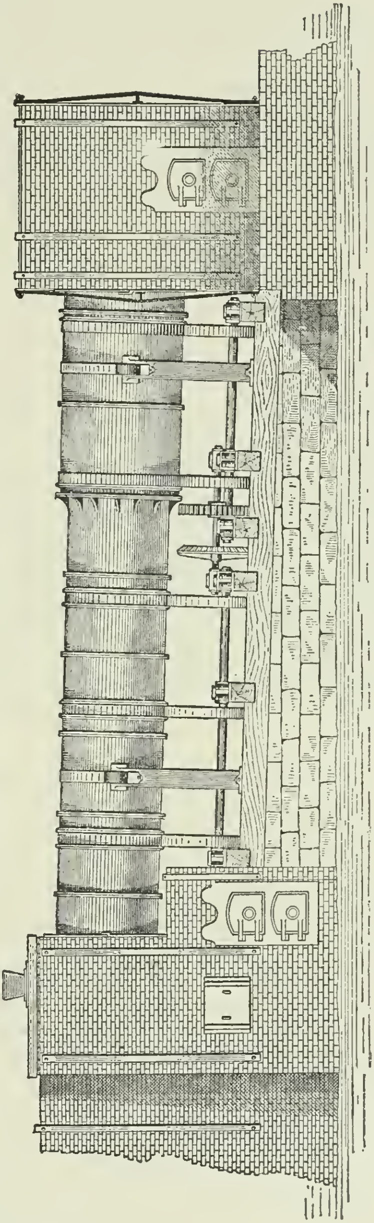

Fig. 20.—White-Howell Furnace.*

The White-Howell Furnace (Fig. 20) is similar in construction to the White furnace, but differs from it in the following particulars :—

The iron shell is enlarged in the part nearest the fire-box in order that it may be lined with fire-brick, and this is the only part of the furnace which is lined. Fire-brick ledges project from this lining as in the White furnace, but are arranged spirally and not longitudinally. Cast-iron ledges are also fitted spirally to the unlined portion of the shell. In both furnaces there is sometimes an auxiliary fire at the dust chamber for roasting the dust which is carried over.

The Argall Furnace.—This furnace was devised by Mr. Philip Argall for roasting Cripple Creek ores for cyanide treatment. It consists of four small iron cylinders lined with fire-brick instead of one large one.

The cylinders are about 30 feet long by 2 feet in diameter, and are bound together by two steel tires which rest on friction wheels driven by gearing. The upper and lower ends are enclosed by cylindrical heads, the upper receiving the raw ore and feeding it into the cylinders, and the lower discharging the roasted ore.

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* Rose, *Gold*, p. 236.

The ore is evenly distributed between the four cylinders, so that the furnace is evenly balanced and requires only 1 H.P. to drive it. The furnace is set at a slight inclination, which is varied according to the time required for roasting. There is the usual fire-box at the lower end and a dust chamber at the upper, but little dust is produced. The furnace revolves about once in four minutes, and its capacity, when roasting ores containing 2 per cent. sulphur, is from 45 to 50 tons per day, the sulphur being reduced to 0·1 per cent. For pyritic ores containing 12 per cent. sulphur its capacity is said to be from 25 to 30 tons per day.*

IV. **Muffle Furnaces.**—The most important type of muffle furnace is the Hasenclever furnace, which is used to a considerable extent in roasting zinc blende, for the utilization of the SO_2 produced in the manufacture of sulphuric acid. It is shown in section in Fig. 21.

According to Ingalls † it is the simplest, and perhaps the most efficient, hand-worked muffle furnace for the above-mentioned purpose, at least, it is the most generally used in Europe, but is gradually being displaced by others (see pp. 473-479). The furnace consists of three muffles superposed, with a fire-box with a step or ordinary grate at one end. They are built in pairs, or in blocks of four. The muffles are constructed of fire-brick and special fire-tiles, and the flame and furnace gases pass under and over each, then by a downtake to the flue leading to the chimney-stack.

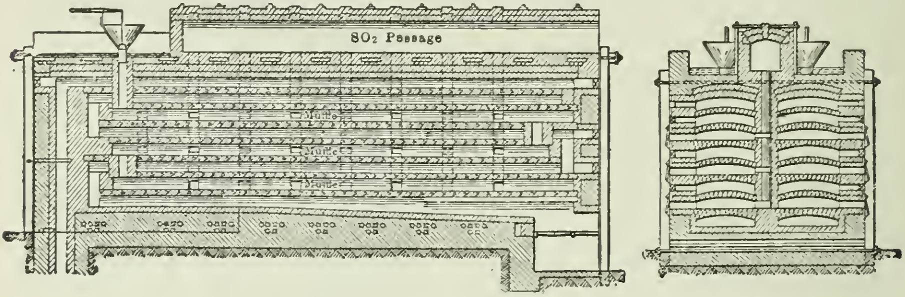

Fig. 21.—Hasenclever Furnace.‡

The ore is charged through a hopper into the uppermost muffle, and is worked by rabbles along the hearths, in the opposite direction to the flame outside, to the openings at the extremity of each. It is thus made to pass from one muffle to the other, and is finally drawn from the lowest muffle through a door at the further end. The SO_2 produced passes through openings in the sides of the muffles into vertical flues leading to the main flue, by which it is led to the sulphuric acid chambers. In some of the furnaces the air for oxidation is heated in flues below the flue leading from the fire-place.

The capacity of the furnace is about 4 to 4½ tons of blende in twenty-four hours, the roasted product containing about 1 per cent. of sulphur.

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* Rose, *Gold*, p. 237.

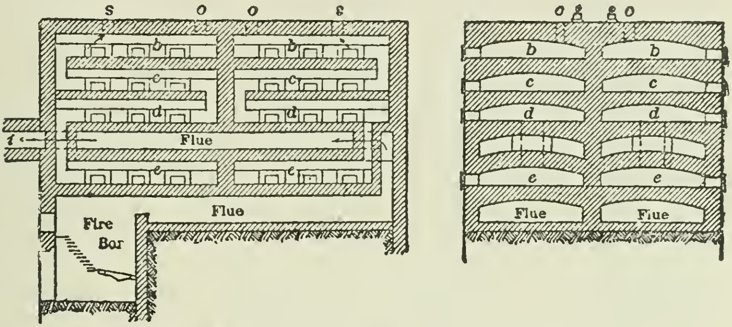
† Ingalls. *The Metallurgy of Zinc*, p. 131.

‡ *Eng. and Min. Journ.*, March, 1912.

In recently constructed furnaces there are four superposed muffles, each 41 feet long, 5 feet broad, 9 inches high at the centre, and each is divided by a transverse wall into two sections (Figs. 22 and 23). The SO_2 passes through all the muffles and out through an aperture in the roof of the top muffles.

When the ores are rich in sulphur the flame from the fire-place passes under the lowest muffle, then over it heating the bottom of the muffle above and then passes into the chimney flue. The two upper muffles derive their heat from the oxidation of the blende. These modifications have resulted in an increased output and a diminution in the fuel consumption. The advantages of the Hasenclever furnace as compared with the ordinary reverberatory are that a gas very much richer in SO_2 is obtained and the fuel consumption is less.

Shaft Furnaces are also employed in roasting, and there are many varieties, the most important being the Stetefeldt furnace.



Figs. 22 and 23.—Hasenclever Furnace—Sections.*

The Stetefeldt Furnace (Fig. 24).—Its chief use was for the chloridizing-roasting of silver ores, and until recently it was extensively employed, but the changes in the metallurgy of silver, which have led to the disuse of this process in several localities, have greatly diminished the number of these furnaces in operation, and they will probably soon become obsolete.

The furnace consists of a perpendicular shaft B slightly tapering upwards, heated by two fire-places or gas at G G, with a descending flue H also heated by a gas-fire E. Its height varies from 30 to 45 feet, the higher furnaces being used when the ores contain more sulphur than usual, or a large output is required. The shaft is square in section and from 4 to 6 feet wide. At the bottom of the flue is a dust chamber D to catch the dust, which is carried over in considerable quantities, and is discharged from time to time through the hoppers F F into trucks. At Q Q are doors to admit air, and to allow tools to be introduced to remove any ore which may have become attached to the walls. The shaft is built of two 9-inch brick walls with a 3-inch air space between them. The gas generators, fire-box, bridges, and lower part of the shaft are of fire-brick, the other parts of red brick.

The ground ore, mixed with salt, when chloridizing-roasting is practised, is fed into the top of the shaft by a special feeder, is showered down through the flame from the two fires on each side, and falls into the cast-iron hopper at the bottom. This is closed by a door which is opened from time to time to discharge the roasted ore into cars by which it is taken to the cooling floor, where it is left in heaps for one or two days. This increases the chloridization, often as much as 30 or 40 per cent.

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* Ingalls, *op cit.*, p. 139.

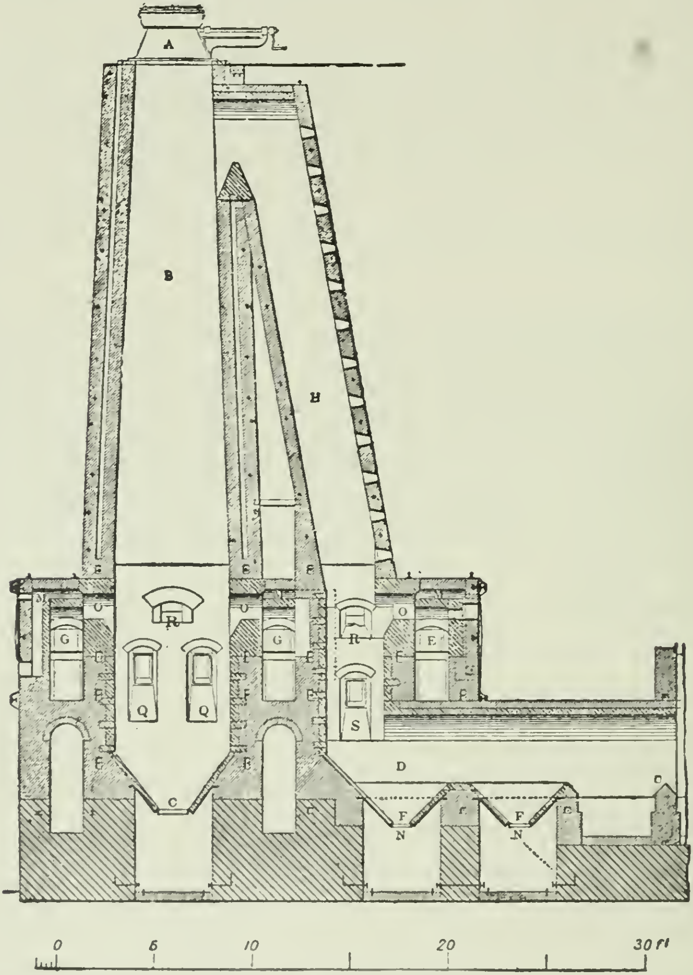

Fig. 24.—Stetefeldt Furnace.*

The dust carried over into the downtake flue is roasted and chloridized by the auxiliary fire, and is allowed to remain in the hoppers of the dust chamber, as long as possible, to become further chloridized.

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* Roberts-Austen, *op. cit.*, p. 346.

The feeder consists of a fixed iron plate with fine punched holes, above which is a wire screen of about ¼-inch mesh forming the bottom of a wrought-iron box, which is made to oscillate about 3 inches backwards and forwards. The ore in the box is kept in motion by fixed stirrers, passes first through the wire screen, then through the perforated plate, and is thus satisfactorily distributed over the whole area of the shaft. The capacity of the large furnaces is about 40 to 70 tons in twenty-four hours, but this depends on the percentage of sulphur in the ore. The furnace is, however, only suitable for the so-called "light ores," those containing less than 8 per cent. of sulphur. If the ore contains over 10 per cent. of sulphur the roasting is imperfect.

The advantages of the Stetefeldt furnace are :—

1. The cost of labour and the consumption of fuel are low.

2. It has a large output when working on ores containing less than 6 per cent. of sulphur.

3. The dust produced is well chloridized.

Its disadvantages are :—

1. Inability to roast satisfactorily ores with more than 10 per cent. of sulphur.

2. Unsuitability for ores containing much galena or galena and blende. Zinc blende is very imperfectly roasted. The particles of galena fuse on their exterior and the oxidation of the interior is prevented.

Another kind of shaft furnace for roasting is the *Gerstenhöfer furnace*, which was designed for roasting fine pyritic copper ores without fuel and for the utilization of the SO_2 produced for the manufacture of sulphuric acid. It is in use at but few works at present, and is becoming obsolete, and hence requires only a brief notice.

It consists of a rectangular shaft 4 feet 6 inches by 2 feet 8 inches in horizontal section and 12 to 16 feet in height, across which are fixed 15 or 17 rows of narrow shelves of fire-clay triangular in section with the broad side uppermost. The rows are formed alternately of six or seven shelves. In the front wall of the shaft are rows of openings at the ends of the shelves for cleaning and changing them. The air for oxidation is admitted through apertures near the base of the shaft.

In starting the furnace, grate bars are put in temporarily, upon which a fire is made, and the firing is continued until the furnace is red-hot. When at a bright red heat, ore is charged in and the fire is kept up until the lower shelves are beginning to receive the ore. The grate bars are then withdrawn, the oxidation of the sulphur generating sufficient heat for the roasting. The ore is fed through fluted rollers, falls from shelf to shelf, meeting the air which has been admitted for oxidation, until it reaches the bottom of the shaft, whence it is withdrawn through a side door. For the satisfactory working of the furnace the ore must contain, at least, 25 per cent. of sulphur, as if less is present a supplementary fire-place is required and the SO_2 cannot be utilized.

The disadvantages of the furnace are that the ore is but imperfectly roasted, about 5 per cent. of sulphur or more remains in the product, and much flue dust is produced.

Its capacity is 3 to 5 tons of pyrites, containing about 40 per cent. of sulphur, in twenty-four hours, leaving about 6 per cent. of sulphur in the roasted ore.

Nodulizing.—This operation has been introduced for the treatment of flotation concentrate at several smelters (see p. 138). The extreme fineness of the concentrate gives rise to very great losses by dusting when subjected to ordinary roasting processes, and when it forms part of the charge of a blast furnace. Briquetting with the addition of lime or flue dust is in use at one or two smelters, but the briquettes break up and produce much flue dust before they are smelted.

On the other hand, nodulizing is said to give an excellent product for smelting with small loss by dusting.

The operation is carried on in revolving cylindrical furnaces of the White-Howell type about 100 feet long, 7 feet in diameter, and sloping 1 inch to the foot, oil or powdered coal being used as fuel.

At Braden, with the temperature of the furnace at 825° C., the concentrate assumes a sticky consistence, and the rolling motion causes it to ball into nodules.

When the product is required for pyritic or semi-pyritic smelting, it is necessary to retain as much sulphur in the charge as possible, the rotary furnace is then built with a seal at the discharge end, so as to limit the entrance of air over and above that necessary to burn the fuel.

When low sulphur is desired in the product and air is freely admitted, the concentrate is mixed with a refractory diluent (which may be silica, siliceous ore, or limestone), to separate the fine sulphide particles, prevent their fusion, and allow them to roast before reaching the nodulizing zone.

Nodulizing is also practised to prepare flotation concentrate for treatment on Dwight-Lloyd machines.

FLUXES AND SLAGS.

Fluxes.—In smelting the term "fluxes" is applied to the materials which it is necessary to add to the furnace charges, in order that the gangue and earthy matter of the ore may be fused and a suitable slag produced. In some ores the gangue is fusible itself, these ores are termed "self-fluxing," and no addition of other material is needed in smelting them. Such ores are, however, somewhat scarce. The chief fluxes commonly employed in smelting the ores of the non-ferrous metals are iron oxides, calcium carbonate as limestone, silica as siliceous ores, etc., and occasionally fluorspar.

In all cases ores containing these, together with one or more of the useful or valuable metals which can be extracted in the smelting operations, should be used as fluxes whenever procurable. Barren fluxes should be avoided if possible, as it costs as much to smelt a ton of flux as a ton of ore; and besides they increase the quantity of slag produced, the amount of metal which may be carried off in it, and the cost of labour in disposing of it.

Iron Oxides are extensively used in the smelting of the usual siliceous copper, lead, and silver ores. The most advantageous form in which they can be obtained is as the gossan of ore deposits, as they generally contain small amounts of copper or lead, and often gold and silver. When these are not procurable, hæmatite or other iron ore may be employed.

"Burnt" pyrites from sulphuric acid works, containing small amounts of copper, may be used as a flux in the smelting of copper ores.

Iron oxide yields very fluid slags with silica, and the larger the amount, within reasonable limits, up to 69 per cent. FeO, the greater will be their fusibility, but the higher their specific gravity. In actual practice this high percentage of FeO is never used, as the silicate formed would have such a high specific gravity that a clean separation of copper matte or lead from it would not be possible. It would also have a very corrosive action on furnace linings.

Iron oxide, although indispensable in copper and lead smelting, is never used alone, more or less lime must always be present, or be added.

In copper smelting the FeO generally ranges from 25 to 50 per cent. and the CaO from 12 to 25, with SiO_2 from 32 to 40 per cent.

In lead smelting the FeO may range from 24 to 52 per cent., and the CaO from 0 to 30 per cent., with SiO_2 from 28 to 36 per cent.

In copper smelting, if FeO only is available as a base, the SiO_2 contents should be about 38 per cent. for blast-furnace and 42 per cent. for reverberatory-furnace work.

The addition of lime to a ferrous silicate slag lowers its specific gravity, increases its fusibility, and, according to Peters, lessens the dissolving power of the slag for metallic sulphides.

The extent to which CaO may replace FeO is important. Iron singulo-silicate, $2FeOSiO_2$, melts at 1,270° C., but by the gradual replacement of FeO by CaO the melting point is lowered, so that with 16 per cent. CaO and 53 per cent. FeO it is reduced to 1,170° C., whilst with 28 per cent. CaO and 40 per cent. FeO the melting point is also 1,170° C. But it is rarely that a slag consists solely of FeO, CaO, and SiO_2, as other bases such as MgO, Al_2O_3, ZnO, and BaO are usually present.

The low melting point of slags, especially the bisilicates, is not always an advantage, as they are more or less viscid and sluggish in flowing, the furnace works slowly and the matte or metal does not separate satisfactorily.

In lead smelting, iron oxides, which are reduced to FeO in the blast furnace by CO, not only act as a flux, but also decompose any lead silicate which may be present, setting free PbO which is reduced to metal by the coke. Part, too, is reduced to metallic iron, and this decomposes lead sulphide with the separation of metallic lead.

Limestone as a flux for the siliceous gangue of copper, lead, and other ores is preferably used in the form of calcareous ores when these are obtainable, otherwise the crushed rock has to be employed.

The use of caustic lime instead of limestone has been tried at several works, but the saving of fuel which it was expected would result, if the blast-furnace was relieved from the work of decomposing the carbonate, has not been realized in actual practice.

"It may be said that, apart from FeO—a certain amount of which is absolutely indispensable to promote the fusibility of all ordinary copper and lead slags—CaO is our most universal and advantageous flux for silica, that it may be used freely and without special precautions until it forms (together with MgO) some 25 per cent. of the weight of the resulting slag, provided always that, in reaction smelting (partial pyritic smelting), the percentage of FeO does not fall below 20, and the SiO_2 does not rise above 40 per cent., or the SiO_2 plus Al_2O_3 above 46 per cent. In straight coke smelting the ferrous oxide may drop a few per cent. lower, and the silica and alumina rise a few per cent. without experiencing trouble."*

It is important that the limestone for fluxing purposes should be free from silica or silicates, or, at least, should contain them only in small proportions, as its chief function is to combine with and slag the silica of the ore. Pure calcium carbonate contains 56 per cent. of CaO, so that 179 parts of limestone must be used for every 100 parts of CaO required for fluxing. A very small amount of silica diminishes the fluxing power. Thus, if 35 parts of silica require 100 parts of pure limestone, and the limestone to be used contains only 5 per cent. of silica, 121 parts of it would be required.

The limestone is never used as a flux alone, but always with more or less iron oxides. As, however, it is cheaper usually than iron flux, and besides, for a given weight, neutralizes more silica, and therefore produces less slag, a large proportion is generally used up to 30 per cent. of CaO in the slags, more particularly in lead smelting.

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* Peters, *Practice of Copper Smelting*, p. 631.

Magnesian or dolomitic limestones are not so satisfactory as fluxes, as the MgO gives rise to pasty slags. This is especially noticeable in lead smelting, but in copper smelting also, even in modern furnaces, if the MgO exceeds 10 or 12 per cent., the slags tend to become refractory and flow sluggishly.

Silica as a flux is used in the form of quartz, quartzite, and sandstone.

Siliceous ores are also available, but as regards these it must be remembered that it is only the free silica they contain that is effective. The silica combined with CaO, FeO, or other bases, is useless, as it is already saturated. For the same reasons siliceous slags are only useful for the excess of free silica present.

In lead smelting silica is usually employed in the form of siliceous silver ores when the gangue is basic and ferruginous.

In the pyritic smelting of copper ores silica is essential, and must be as pure as possible, as quartz, sandstone, and the like, containing the maximum amount in the free state, to combine at once with the FeO as it is formed.

It is also necessary, and is largely employed, in the concentration of copper mattes by pyritic smelting and in the conversion of mattes in the basic Bessemer converter.

Fluorspar.—Its melting point is about 900° C. When molten it is extremely fluid, hence it is valuable in smelting for increasing the fluidity of slags. It also forms fusible compounds with barium and calcium sulphates, and assists in fluxing zinc either as sulphide or oxide. It is the best flux for bone ash in smelting cupels and cupellation hearths composed of that material; and is also used as a constituent of the electrolytic bath employed in the manufacture of aluminium.

Apart from its power of fluxing the substances just mentioned, fluorspar is specially important for its property of conferring fluidity on slags, and in this it appears to act to a great extent mechanically, as a great part of it is found unchanged in them.

Alkaline Fluxes.—These are too expensive for use in ordinary smelting, hence their employment is confined to the processes of assaying and special operations in the metallurgy of bismuth, antimony, etc.

Slags.—The silicates formed in smelting and other metallurgical processes by the combination of silica with the earths and metallic oxides are termed "slags." With the exception of the slags produced in a few metallurgical operations, such, for example, as the smelting of bismuth and antimony ores, the refining of lead, etc., and the processes of assaying, all slags are silicates.

The composition of slags is usually very complex, but the chief bases present are FeO, CaO, Al_2O_3, MgO, with sometimes ZnO, BaO and MnO, also generally more or less of the oxides of the metals that are being smelted.

Silicates are classified according to the ratio which exists between the oxygen in the base and in the acid.

The silicate $2FeO + SiO_2$ is termed a monosilicate, unisilicate, or singulosilicate, there being equal amounts of oxygen in the base and acid, whilst the silicate $FeO + SiO_2$ is termed a bisilicate, as there are two atoms of oxygen in the acid to one atom in the base, and so on.

In the following table of the series of formulæ for silicates the letter R is used to indicate any one or more of the metals whose oxides form the bases which are found in slags :—

TYPES OF SILICATES.

Formula.	Oxygen in Base.	Oxygen in Acid.	Name.
$4RO + SiO_2 = R_4SiO_6$, . .	2	1	Subsilicate
$2RO + SiO_2 = R_2SiO_4$, . .	1	1	Monosilicate
$4RO + 3SiO_2 = R_4Si_3O_{10}$, .	2	3	Sesquisilicate
$RO + SiO_2 = RSiO_3$, . .	1	2	Bisilicate
$2RO + 3SiO_2 = R_2Si_3O_8$, . .	1	3	Trisilicate

A sesquisilicate may be regarded as a mixture of a monosilicate with two parts of bisilicate, thus—

$$4RO + 3SiO_2 = 2RO + SiO_2 + 2(RO + SiO_2).$$

As a rule, other things being equal, the subsilicates are more fusible than the monosilicates, the monosilicates more fusible than the bisilicates, and the bisilicates than the trisilicates—*i.e.*, the fusibility of a silicate decreases as the proportion of silica increases. But their relative fusibility also depends on the bases present—for example, a bisilicate of CaO and BaO is practically infusible at furnace temperatures ; on the other hand, a bisilicate of FeO and CaO is quite fusible.

The slags in copper smelting lie between the two extremes, monosilicates and bisilicates, whilst in lead smelting they are monosilicates, although sesquisilicates are sometimes made. Their contents in silica in copper smelting range from 30 to 44 per cent. ; according to Peters, about 38 per cent. should be aimed at for blast-furnace work and 42 per cent. for reverberatory smelting.

In lead-smelting slags the silica ranges from about 28 to 36 per cent.

If a silicate contains only one base it is termed a monobasic or simple silicate. If two or more are present it is termed a double, multibasic, or polybasic silicate.

The bases which commonly occur in ordinary slags are FeO, MnO, CaO, Al_2O_3, MgO, and BaO, the iron and manganese silicates being the most fusible. The earthy silicates are only fusible at very high temperatures, but in some cases as double silicates they have lower melting points, as, for example, the bisilicate Al_2O_3, 3CaO, $6SiO_2$, which melts at 1,300° C. Alumina, however, is objectionable in smelting the non-ferrous metals for the reasons given later, and FeO is the base always added to lower the melting points of the earthy silicates.

The following tables by Balling show the relative equivalent values of the principal bases which combine with silica to form silicate slags :—

TABLE A.

For ascertaining the necessary amounts of Bases to convert given amounts of Silica into slag.

One Part by Weight of Silica requires—	Parts by Weight of Bases.
For Monosilicates—	
Lime,	1·86
Magnesia,	1·33
Alumina,	1·14
Ferrous oxide,	2·40
Manganous oxide,	2·36
For Bisilicates—	
Lime,	0·93
Magnesia,	0·66
Alumina,	0·57
Ferrous oxide,	1·20
Manganous oxide,	1·18
For Sesquisilicates—	
Lime,	1·24
Magnesia,	0·88
Alumina,	0·76
Ferrous oxide,	1·60
Manganous oxide,	1·57

TABLE B.

For ascertaining the necessary amounts of Silica to convert given amounts of Bases into slag.

One Part by Weight of Base requires—	Parts by Weight of Silica.
For Monosilicates—	
Lime,	0·535
Magnesia,	0·750
Alumina,	0·873
Ferrous oxide,	0·416
Manganous oxide,	0·422
For Bisilicates—	
Lime,	1·070
Magnesia,	1·500
Alumina,	1·747
Ferrous oxide,	0·833
Manganous oxide,	0·845
For Sesquisilicates—	
Lime,	0·803
Magnesia,	1·125
Alumina,	1·310
Ferrous oxide,	0·625
Manganous oxide,	0·633

The qualities required in a good slag are :—

1. Its formation temperature must be low, but sufficiently high for carrying out the reactions required in the smelting operations.
2. It must be sufficiently fluid to flow freely from the blast furnace, but in reverberatory smelting its consistency should be such that it can be conveniently skimmed clean from matte or metal.
3. Its specific gravity should be sufficiently low to allow globules of matte or metal to settle through it readily and completely, so that it may contain the lowest practicable amount of these. For the same reason its viscosity should be low.
4. It should be produced at the lowest cost of fluxes and fuel.

As regards the formation temperature of a slag, it must be borne in mind that this is generally considerably lower than the temperature at which the slag is sufficiently fluid to flow freely. Thus the bisilicates first pass through a state of viscous semi-fusion before they attain sufficient liquidity to flow freely. In these cases it is necessary to raise the temperature considerably above their softening point before they will flow properly, and this requires an extra consumption of fuel.

The formation temperature of a slag bears no definite relation to its flowing temperature.

Hence it follows that the viscosity or resistance to flow of a slag is as important in smelting as its melting point; in fact, its free-running temperature is the critical temperature of a blast furnace.

The viscosity of slags formed in smelting the non-ferrous metals, *cæteris paribus*, increases with the silica. It is also increased by the presence of alumina and zinc oxide.

It has not been definitely determined whether alumina acts as a base, or as an acid, or as both, according to the composition of the slag. It is certain, however, that when more than 8 or 10 per cent. is present it seriously increases the viscosity of slags.

Zinc oxide has an especially pernicious effect if the percentage of iron is low. According to Peters, 12 per cent. of zinc oxide is the extreme limit permitted in the slags from copper blast furnaces, although this is sometimes exceeded a little in pyritic smelting and in the reverberatory.

In lead smelting—" When the proportion of zinc oxide rises above 10 per cent. all ordinary slags become pasty and tend to form accretions above the lead. With a monosilicate slag, according to Hofman, 16 per cent. is the maximum amount of ZnO with which it is possible to run, but Greenway has found that over 20 per cent. of ZnO can be run without difficulty, provided the slag be rich in iron and that SiO_2 and CaO be kept within very narrow limits, those for the former being between 23½ and 26 per cent., and for the latter between 12 and 16 per cent." *

Another nomenclature of slags which depends on the ratio of the CaO to FeO is in frequent use in lead smelting.

Thus, a slag in which the CaO is one-fourth of the FeO is termed a *quarter* slag, whilst if it is one-half of the FeO it is termed a *half* slag.

These terms are illustrated in the following table of lead slags, all of which are in use in lead smelting:—

FORMULÆ AND COMPOSITION OF TYPICAL MONOSILICATE LEAD SLAGS.†

Formulæ.	SiO_2.	FeO.	CaO.	Total.
1. " *Quarter* " *Slag.*				
$3[2FeO . SiO_2]$, $+ 2CaO . SiO_2$, . . . }	30·6	55·2	14·2	100
=	26	47	12	85
Add 5 per cent. SiO_2, . .	31	47	12	90
In practice, ...	30	48	12	90
2. " *Half* " *Slag.*				
$3[2FeO . SiO_2]$. $+ 2[2CaO . SiO_2]$, . . . }	31·4	45·2	23·4	100
=	27	38	20	85
Add 5 per cent. SiO_2, . .	32	38	20	90
In practice, ...	32	38	20	90
3. " *Three-quarter* " *Slag.*				
$2FeO . SiO_2$, ... $+ 2CaO . SiO_2$, . . . }	31·9	38·3	29·8	100
=	27	33	25	85
Add 5 per cent. SiO_2, . .	32	33	25	90
In practice, ...	33	33	24	90
4. *1 : 1 Slag.*				
$3[2FeO . SiO_2]$, $+ 4[2CaO . SiO_2]$, . . . }	32·3	32·3	34·4	100
=	28	28	29	85
Add 5 per cent. SiO_2, . .	33	28	29	90
In practice, ...	34	28	28	90

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* Collins, *Lead*, p. 158.

† Collins, *Lead*, p. 157.

COPPER.

Physical Properties.—Copper is distinguished by its red colour from all other metals.

Malleability and Ductility.—It can be rolled into very thin sheets, beaten out into leaves and drawn into fine wire, and thus possesses the properties of malleability and ductility in a high degree. By cold rolling or other mechanical treatment it becomes hard, but its malleability is regained by annealing. It is immaterial whether the copper be quenched in water or cooled slowly after the annealing process.

Tenacity.—Its tenacity when cast is 8 to 10 tons per square inch ; when rolled or drawn 16 to 23 tons or even more, according to the amount of mechanical treatment it has received.

Specific Gravity.—The specific gravity of pure copper, rolled, forged, or drawn, and afterwards annealed, may be taken as 8·89 at 20° C.,* but that of ordinary commercial copper usually ranges from 8·2 to 8·8, the lower figures being due to porosity.

Action of Heat.—The melting point of copper lies somewhere about 1,083° C. When molten it is rapidly oxidized with the formation of cuprous oxide (Cu_2O), which dissolves in the metal. It also absorbs hydrogen and sulphur dioxide, which are given off during solidification : part, however, remains in the metal, producing more or less porosity. Hence arises the difficulty of obtaining sound castings of copper.

The metal is not volatilized at the temperature of ordinary furnaces, but readily in the electric furnace at temperatures above 1,650° C. ; its boiling point is about 2,100° C. (Moissan). When heated to near its melting point it becomes so brittle that it may be easily powdered.

Electrical Conductivity.—As a conductor of electricity copper is only surpassed by silver, and hence is largely used for electric wires and cables.

Its electrical conductivity is 976 if silver be taken as 1,000. This is greatly reduced by the presence of impurities, especially by cuprous oxide, phosphorus, arsenic, antimony, and silicon. It is also reduced by cold working.

The International Standard of *Electrical Resistance* for annealed copper is 0·15328 ohm at 20° C. for a wire 1 metre in length and weighing 1 gramme. This is equivalent to a *Resistivity* of 1·7241 microhms per centimetre cube.†

Conductivity for Heat.—Copper is an excellent conductor of heat, and in this property is only surpassed by silver.

Atomic Weight.—63·57.

Chemical Properties.—Copper undergoes certain changes when exposed to the atmosphere at ordinary temperatures,‡ films being formed on the surface which vary according to the purity of the atmosphere, and especially as regards the presence of moisture and sulphuretted hydrogen. When heated to redness with access of air, as in annealing sheets, etc., a dark coloured scale is formed, which consists almost wholly of cuprous oxide. It may be removed by plunging the copper whilst red hot into cold water; in practice the water used contains sulphuric acid. Copper is slowly dissolved by weak acids in the presence of air. It is soluble in nitric acid, aqua regia, and in hot concentrated sulphuric acid.

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* Circular of the Bureau of Standards (U.S.A.), No. 73, Copper, p. 38.

† Smithsonian Physical Tables, 1923, p. 334.

‡ See reports to the Atmospheric Corrosion Committee, *Trans. Faraday Soc.*, 1924, 19, 839 ; 1927, 23, 113 ; 1929, 25, 177. W. H. J. Vomon and L. Whitby, *Journ. Inst. Metals*, 1929, xlii., 181.

Copper Oxides.—There are two oxides of copper—viz., red or cuprous oxide (Cu_2O) and black or cupric oxide (CuO).

Cuprous oxide is readily fusible at furnace temperatures, and at a red heat is easily reduced by hydrogen, carbon monoxide, charcoal or other carbonaceous matters, and by iron, zinc, and metals having a strong affinity for oxygen. When heated with iron sulphide or cuprous sulphide it is reduced to metallic copper, according to the following equations:—

$$3Cu_2O + FeS = 6Cu + FeO + SO_2.$$
$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

Cupric Oxide.—This oxide is as easily reduced as cuprous oxide and by the same reducing agents, but it is not fusible.

Copper Sulphides.—There are two copper sulphides—viz., cuprous sulphide and cupric sulphide, but only the former is of importance in metallurgy.

Copper has a strong affinity for sulphur, and on this affinity the extraction of copper from its ores by smelting is largely based.

Cuprous Sulphide, Cu_2S.—Cuprous sulphide is a black or bluish-grey substance, and melts at about 1,130° C.

A knowledge of the properties and behaviour of cuprous sulphide under varying conditions is of the first importance in the metallurgy of copper for the proper understanding of the processes of smelting and for satisfactorily carrying them out.

Cuprous sulphide undergoes no change when strongly heated without access of air. When ground and gradually heated to incipient redness with access of air, both the sulphur and copper are oxidized, part of the sulphur being converted into sulphur dioxide and part into sulphuric acid. The former escapes as gas and the latter combines with some of the copper oxide, forming copper sulphate.

If the temperature now be raised to a strong red heat the copper sulphate will be decomposed, and the product will consist entirely of cupric oxide. If cuprous sulphide be heated to the melting point of copper in admixture with cuprous oxide, cupric oxide, or copper sulphate, in such proportion that the sulphur and oxygen exist in the ratio in which they exist in sulphur dioxide, the whole of the sulphur will be evolved as sulphur dioxide and metallic copper will remain. When the oxygen exceeds this ratio a proportionate amount of Cu_2O will remain in the product. When the sulphur exceeds this ratio the product will contain a proportionate amount of Cu_2S.

The reactions which occur are expressed in the following equations:—

1. $Cu_2S + 2Cu_2O = 6Cu + SO_2.$
2. $Cu_2S + 2CuO = 4Cu + SO_2.$
3. $Cu_2S + 3CuO = 3Cu + Cu_2O + SO_2.$
4. $2Cu_2S + 2CuO = 4Cu + Cu_2S + SO_2.$
5. $Cu_2S + CuSO_4 = 3Cu + 2SO_2.$
6. $Cu_2S + 2CuSO_4 = 2Cu_2O + 3SO_2.$

These reactions are of great importance in the smelting of copper ores and the Bessemerizing of mattes.

Cuprous sulphide when heated with carbon is not reduced. Carbon monoxide has no action on it at a red heat.

When heated with iron it is only partially reduced to the metallic state, a double sulphide of copper and iron being formed upon which iron has no reducing effect.

When melted with other metallic sulphides it unites with them, forming mattes.

Copper Silicate.—When copper oxides are heated with silica, copper silicates are formed, hence in smelting oxide ores in the absence of sufficient sulphur, copper as silicate may pass into the slag.

The copper contained in refining, roaster, and converter slags exists chiefly as silicate. Copper silicates are decomposed by iron sulphide and by iron as follows :—

$$Cu_2SiO_3 + FeS = Cu_2S + FeSiO_3.$$
$$Cu_2SiO_3 + Fe = Cu_2 + FeSiO_3.$$

They are also reduced by carbon in the presence of iron oxide thus—

$$Cu_2SiO_3 + C + FeO = 2Cu + FeSiO_3 + CO.$$

The extraction of copper from refinery and other silicate slags and from silicate ores is based on the above reactions.

Copper Sulphate, $CuSO_4 + 5H_2O$.—This salt occurs in mine waters, as at Butte, and in the washings of copper ores which have been roasted in heaps, as at Rio Tinto. It is manufactured on a large scale by subjecting granulated copper, and preferably copper " bottoms " or copper containing gold and silver, to the action of dilute sulphuric acid, steam, and air in towers lined with lead, and crystallizing the solutions. The precious metals settle in the form of mud in the solution vats. Copper sulphate is also produced as a by-product in parting gold and silver by the sulphuric acid process, and in the Ziervogel and other operations. The copper is obtained from it by precipitation by iron or by electrolysis.

Commercial Copper.—The following are the chief kinds :—

" Standard " copper, formerly G.M.B. or " good marketable brands," is the basis of trading on the London Metal Exchange.

By it is meant any unrefined copper, such as " Chili bars " containing not less than 97 per cent. copper, and certified to be " good marketable " —*i.e.*, not containing excessive amounts of injurious impurities.

If the percentage of copper falls below 97 a *pro rata* allowance is made in the price per ton, but no excess is paid for.

Tough Cake and Ingot.—This is refined copper less pure than the following kinds, but suitable for rolling into sheets, drawing into wire, and hammering into pans and the like. It can also be used in the manufacture of brass for ordinary castings which have not to be hammered, rolled, or drawn. The British Standard Specification * requires it to contain not less than 99·2 per cent. copper with not less than 0·3 nor more than 0·5 per cent.

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* *Brit. Eng. Stand. Assoc.*, No. 200, 1924, pp. 1-6.

arsenic. It must give a tensile strength of not less than 14 tons per sq. in. and an elongation of not less than 35 per cent.

Best Selected Copper.—Any refined copper containing only small amounts of impurities is sold under this name, although it has not been made by the "best selecting" process. It is in extensive use for sheets, tubes, and wire, and for the manufacture of brass and other alloys. The British Standard Specification * for "Best Select" Copper requires a minimum copper content of 99·5 per cent., with the following maxima for impurities :—Arsenic, 0·05 ; antimony, 0·007 ; bismuth, 0·007 ; lead, 0·1 ; iron, 0·025 ; nickel, 0·2 ; sulphur, 0·005 ; zinc, 0·005 ; tin, 0·005. When the copper content is not less than 99·7 per cent., it is permissible for the antimony, bismuth and sulphur to be 0·025, 0·02 and 0·02, respectively. The maker's brand must be stamped or cast in.

Lake Copper.—By this name is understood refined copper produced from Lake Superior ores.

It is exceptionally pure. It commands the highest price in the London market, sometimes even exceeding that of electrolytic copper ; this is partly due to its reputation, and partly to the occasional occurrence of sulphur in the latter, which tends to produce defective castings when used for the manufacture of alloys.

When obtained from surface ores which were remarkably free from impurities, Lake copper was of the highest electrical conductivity. As the depth of the deposits increased, arsenic began to appear, and at the works of one of the companies the copper is refined electrolytically, the product still being classed on the market as "Lake," although it is equally electrolytic (Addicks).†

Electrolytic Copper.—This is sold both in the form of cathodes, and of ingots and wire bars obtained by melting the cathodes in a refining furnace.

It is especially valuable for wires and leads for electrical purposes on account of its high electrical conductivity.

It is not advisable to use it in the form of cathodes for the manufacture of brass, as these sometimes contain $CuSO_4$, which during melting is decomposed with the formation of SO_2, and unsound castings may result.

The cathodes should always be first treated in a refining furnace before being used in the manufacture of alloys.

Copper Precipitate (*cement copper*) is more or less impure copper which has been precipitated from copper bearing solutions.

It is produced on an extensive scale at the Rio Tinto, Tharsis, and other mines, the product containing arsenic and iron often in considerable amounts.

In the table which follows is given the composition of typical examples of the various kinds of commercial copper.

Influence of Foreign Elements on the Properties of Copper.—The chief foreign elements which occur in commercial refined copper are oxygen, lead, arsenic, antimony, bismuth, and nickel, also sometimes sulphur, iron, tin, zinc, tellurium, and selenium, but the latter are not often present in more than traces.

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* *Brit. Eng. Stand. Assoc.*, No. 203, 1924, pp. 1-3.

† *Eng. and Min. Journ.*, Oct. 1914.

COMPOSITION OF VARIOUS KINDS OF COMMERCIAL COPPER.

	Cu.	Pb.	As.	Sb.	Fe.	Bi.	Ni.	S.
"Standard" bar,	98·70	0·20	0·05	0·06	0·10	trace	0·07	0·85
Tough ingot,	99·44	0·165	0·060	0·005	0·009	0·004	0·173	..
Fire-box plate,	99·20	0·05	0·54	0·006	0·02	0·007	0·09	..
Best selected ingot,	99·67	0·10	0·017	0·004	0·010	0·005	0·10	..
Best selected ingot,	99·71	0·05	0·025	trace	0·007	0·01	0·05	..
Lake wire bar,*	..	0·0014 to 0·0044	trace to 0·007	0·0006 to 0·0052	nil to 0·01	nil	..	..
Cathode copper (not melted),*	..	0·00054	0·00022 to 0·00034	0·00065 to 0·0012	..	..	..	..
Electrolytic wire bar,*	..	trace to 0·00165	0·0007 to 0·001	0·0001 to 0·00019	..	trace to 0·00074	..	..

* Keller, *Mineral Industry*, vol. vii., p. 243.

The effects of each element on the physical properties of copper, as stated below, are diminished or intensified when two or three of the others are present ; thus the injurious effects of lead and bismuth are, to a certain extent, diminished by the presence of 0·5 per cent. arsenic, whilst they are intensified by the presence of antimony.

*Oxygen.**—Copper, when molten, will dissolve cuprous oxide to a very considerable extent, causing a reduction in the melting point of the metal up to 3·5 per cent. Cu_2O, at which point a eutectic of $Cu\text{-}CuO_2$ is formed with a melting point of 1,063° C. Oxygen up to 0·1 per cent. has very little effect on the mechanical properties or on the electrical conductivity of pure copper. When commercial copper contains more than a small but variable amount, depending on the proportions of other metals present, it is said to be " dry " by English copper smelters, and is termed " dry copper." It is then brittle either when cold or hot, and the fractured surface is minutely granular, dull, of a brick-red colour, and without any appearance of fibre. If much cuprous oxide is present, it is of a purplish hue. When cast in an ordinary ingot mould the upper surface of the ingot presents a shallow longitudinal furrow or depression, reaching nearly from end to end along the median line.

When copper, which is smelted on the large scale, is in the highest degree malleable at all temperatures, it is technically said to be at " tough pitch," and if cast in an ordinary ingot mould the upper surface of the ingot is flat without a middle depression or ridge, but with numerous well-defined irregular transverse furrows. The fractured surface of such an ingot, when broken cold, is close-grained, and of a fine salmon-red colour, presenting, especially towards the centre, shining grains of a bright metallic lustre. If this copper is kept melted under charcoal during a sufficient time and then cast into an ingot, the upper surface of the ingot, when solidified, will have a distinct ridge along the median line, broken more or less in extreme cases, owing to " spitting." The metal is brittle, and if broken its fractured surface is uneven, and usually presents small irregular tube-like cavities through which gas appears to have escaped. Its colour is paler than the fractured surface of " tough pitch " copper, and has a somewhat orange hue. Copper in this state is said to be " overpoled." If pure copper, such as electrolytic copper, be thus melted under charcoal, brittleness does not result. From these data the conclusion is inevitable that the brittleness of overpoled commercial copper must depend upon the presence of some foreign matter. It cannot be due to the presence of carbon ; for pure copper may be kept melted any length of time under pure charcoal without becoming brittle. Now, commercial copper is never perfectly free from certain other metals, and amongst those which very frequently occur may be mentioned lead and antimony. Although only a minute quantity of these metals may exist in copper, yet it may be quite sufficient to determine the brittleness of overpoled commercial copper. But " tough pitch " commercial copper must equally contain these metals, and nevertheless is malleable hot as well as cold. However, in " tough pitch " copper there is always present a certain proportion of cuprous oxide which cannot be removed without brittleness resulting. The existence, therefore, of a certain proportion of cuprous oxide in commercial copper would seem to be essential to its malleability (Percy).

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* *Cf.* Hanson, Marryat and Ford, *Journ. Inst. Metals*, 1923, xxx., p. 197.

The brittleness may hence be due to the metals which are present as oxides in tough copper before treatment with charcoal, being innocuous in that state, and only becoming deleterious when they are reduced to the metallic condition.

Oxygen is present in all refined copper and a certain proportion is essential to its toughness and other mechanical properties.

It exists in the copper as Cu_2O, which is practically insoluble in the solid metal, and according to Hampe has no sensible effect on the malleability or tenacity of pure copper until the percentage reaches 0·45. With 0·9 per cent. of Cu_2O ductility in the cold is somewhat diminished.

The percentage of oxygen in arsenical copper is important.* The oxygen concentration should be less than one-tenth of the arsenic concentration in order to obtain metal suitable for severe cold working. Copper containing arsenic and oxygen can be rolled hot without difficulty.

Lead.—Somewhat contradictory results have been obtained in experiments on copper containing lead. According to Lewis, if 0·2 per cent. is present the copper cannot be rolled. Yet Japanese copper containing 0·25 per cent. is regularly hammered into the thinnest vessels, and two excellent fire-box plates contained respectively 0·23 and 0·27 per cent., but in these cases other elements were present in small amounts.

According to Peters, 0·33 per cent. is sufficient to make the metal both red-short and cold-short.

The best brands of English refined copper contain less than 0·1 per cent. lead.

Arsenic.†—When arsenic is present to the extent of 1·0 per cent., it slightly increases the tenacity of copper without diminishing the ductility and malleability, and it has no effect on the Brinell hardness. Such copper can be drawn into the finest wire, and can be rolled without any trace of cracking at the edges. It is, hence, used for fire-box plates and tubes of locomotives, and some engineers specify 0·8 per cent. According to the Specification of the British Engineering Standards Committee not less than 0·35 per cent. nor more than 0·55 per cent. must be present, and the other foreign elements, inclusive of combined oxygen, must not exceed 0·25 per cent. Arsenic seriously diminishes the electric conductivity of the metal. Copper intended for the manufacture of brass which has to be drawn or rolled should not contain more than 0·03 per cent., although good results have been sometimes obtained when 0·05 was present.

Antimony increases the tenacity and hardness of copper, but when present to the extent of 0·2 per cent. the metal will crack at the edges when rolled.

According to experiments by Archbutt, electrolytic copper to which 0·1 per cent. of antimony had been added forged without cracking and bent double at a red heat, and also after annealing bent double cold.

The injurious effects of antimony are, however, chiefly found in cold working. The presence of 0·04 per cent. in copper is liable to give rise to cracks in Muntz metal made from it, and copper containing more than traces should not be used in the manufacture of best brass.

Antimony seriously lowers the electrical conductivity of copper.

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* Hanson and Marryat, *Journ. Inst. Metals*, 1927, xxxvii., p. 144.

† Hanson and Marryat, *Journ. Inst. Metals*, 1927, xxxvii., p. 121.

Bismuth * is the most injurious element which can be present in copper. It tends to increase the tenacity of the metal, but induces such brittleness in both cold and hot rolling, that, according to Laurie, the limiting quantity permissible is less than 0·005 per cent.

In this connection it must be remembered that the injurious effects of bismuth have been shown by Archbutt to be to some extent neutralized by the presence of arsenic. Yet any tough pitch copper containing over 0·01 per cent. of bismuth should be regarded with suspicion.

In copper intended for the manufacture of brass 0·01 is the limit permissible.

Nickel.—In an investigation into the effects of nickel in copper used in the manufacture of brass it was found that Muntz metal made with copper containing 0·3 per cent. rolled better than that made from a number of the best brands of refined copper.

When arsenic is present 0·1 per cent. nickel is said to seriously harden the metal.

Sulphur, iron, tin, and *zinc* should never be present in refined copper, and in fact they rarely occur except in traces.

Sulphur, if in more than traces, is liable to produce unsound castings.

Tellurium is only found in copper from certain districts in America, and a very small amount, according to Eggleston, produces red-shortness.

Phosphorus,† which is sometimes added to copper in order to give soundness to the castings, improves the general mechanical properties of the metal, but has a very deleterious influence upon the electrical conductivity.

The presence of 0·1 per cent. reduces the conductivity to about 60 per cent. of that of pure copper.

Silicon when present in small amounts increases the tenacity of copper without affecting its ductility and malleability. Such copper has hence been used for telegraph and telephone wires, although its electrical conductivity is somewhat lower than that of pure copper. According to Addicks, when 0·042 per cent. is present the conductivity is lowered to 99·0, but according to Johnston 0·01 lowers it to 98·4.

Rarer Metals, etc., frequently present in Blister Copper.—These are removed in the process of refining the copper by electrolysis. The amounts recovered at several electrolytic refineries are given by Eilers as shown on page 61.‡

At Garfield the blister copper comes chiefly from the Bingham porphyry copper mines, and at Steptoe from the Nevada Consolidated porphyry mines. At Omaha the blister comes principally from concentrated copper-lead mattes shipped from the silver-lead plants of the Rocky Mountain region to the converters at the Omaha lead refinery. The Tacoma ores come from Alaska, and are all associated with diorite. The blister at Aguascalientes is produced from the smelting of gold and silver ores with low-grade copper ores, coming from all parts of Mexico and from many different geological occurrences. The Cerro de Pasco ore comes from veins occurring in limestone near andesite masses. No doubt the metals recovered are only a portion of the contents of the ores.

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* See also Hanson and Ford, *Journ. Inst. Metals*, 1927, xxxvii., p. 169.

† C. F. Hanson, Archbutt and Ford, *Journ. Inst. Metals*, 1930, xliii.

‡ Eilers, *Bull. of Amer. Inst. of Min. Engs.*, June, 1913; abstract in *Min. Mag.*, Aug. 1913, p. 141.

Amounts of the Rarer Metals recovered from Blister Copper at several Electrolytic Refineries.

	Blister. Tons.	Gold. Ozs.	Silver. Ozs.	Platinum. Ozs.	Palladium. Ozs.	Selenium. Lbs.	Tellurium. Lbs.	Bismuth. Lbs.	Nickel. Lbs.
Garfield, Utah, . .	5,000	14,400	174,000	17·09	59·14	2,800	277	305	2,000
Per 100 tons blister, .	. .	288	3,480	0·342	1·183	56	5·54	6·1	40
Steptoe, Nevada, . .	3,000	5,070	16,500	30·48	132·10	3,303	None	10	1,920
Per 100 tons blister, .	. .	169	550	1·016	4·402	110	. .	0·33	64
Omaha, Nebraska, . .	800	2,880	184,720	14·60	51·89	213	537	151	7,552
Per 100 tons blister, .	. .	360	23,090	1·825	6·486	26	67·1	18·6	944
Mountain Copper, California,	150	2,127	16,485	1·98	0·91	54	5	41	172
Per 100 tons blister, .	. .	1,418	10,990	1·320	0·607	36	3·3	27·3	11
Tacoma, Washington, .	800	17,496	69,680	5·68	26·62	336	None	46	6,160
Per 100 tons blister, .	. .	2,187	8,710	0·710	3·327	42	. .	5·7	770
Aguascalientes, Mexico, .	1,100	5,302	740,300	4·58	2·49	1,870	None	44	132
Per 100 tons blister, .	. .	482	67,300	0·416	0·226	170	. .	4·0	12
Cerro de Pasco, Peru, .	2,000	3,400	198,000	6·38	11·77	275	None	270	640
Per 100 tons blister, .	. .	170	9,900	0·319	0·589	13	. .	13·5	32
Mt. Lyell, Tasmania, .	800	3,716	57,640	4·99	10·99	336	None	34	1,328
Per 100 tons blister, .	. .	464	7,205	0·624	1·374	42	. .	4·3	166

Alloys of Copper.—In addition to the extensive application of copper itself, it is largely used in the manufacture of alloys. Its alloys, especially those with zinc (the brasses) and with tin (the bronzes), are of vast importance for engineering and other purposes, whilst its alloys with other metals have numerous uses in many industries. When copper is cast in what is termed a closed mould—*i.e.*, a mould with a small aperture or " ingate "—unsound vesicular castings only can be produced. To obtain a sound casting the mould must be an open one, hence none but articles of simple forms can be cast of the metal. This is why alloys of copper have come into such extensive use.

Copper-Zinc Alloys.—These are the true brasses, and to them only should the term " brass " be applied. The following are the chief brasses in industrial use :—

Best Yellow Brass.—Copper 70 per cent., zinc 30 per cent. Largely employed in the manufacture of locomotive and condenser tubes and sheets, also for cartridge cases.

It is the best alloy of the copper-zinc series for any purpose where the metal has to be subjected to severe mechanical treatment, such as rolling or drawing.

Its tenacity is about 28,000 lbs. per square inch.

Ordinary Brass.—Copper 66 per cent., zinc 33 per cent. Frequently substituted for the former, but inferior to it in physical properties.

So-called " cast brass " approximates to this composition, but is usually very variable, and generally contains considerable amounts of impurities, such as tin, lead, and iron. Lead is sometimes intentionally added to this brass when it has to be turned or machined to facilitate these operations.

Muntz Metal.—Copper 60 per cent., zinc 40 per cent. Formerly chiefly used for ship sheathing, now for sheets, rollers for calico printing, amalgamated plates for stamp batteries, and numerous other purposes. It can be rolled and forged hot.

Sterro Metal.—This is merely Muntz metal in which about 1 or 2 per cent. of the zinc is replaced by iron, a harder and stronger metal than ordinary brass being obtained.

It has an extremely high tenacity, 30 tons per square inch, and after rolling this is greatly increased. It was once used for ordnance in Austria, and now for heavy chains for drawbenches and any purposes where a brass of high tenacity only is required.

Delta Metal.—This is an alloy similar to the last. Its average composition is approximately copper 55 per cent., zinc 42 per cent., iron 1 to 2 per cent., and small quantities of aluminium and manganese. It is stronger, harder, and tougher than brass, and is used both for castings and forgings.

Naval Brass.—Approximate composition, copper 62 per cent., zinc 37 per cent., tin 1 per cent. The addition of tin increases the hardness of the copper-zinc alloy, and renders it less liable to corrosion by sea water.

Brazing Solder.—Copper 50 per cent., zinc 50 per cent. It is cast in iron moulds with transverse and longitudinal ridges, so that the cake produced can be readily broken into rectangular pieces.

The solder is prepared for use by heating one of the rectangular pieces in a furnace to a proper temperature. It is then easily reduced to powder in an iron mortar. The grains or powder is then sifted to obtain various grades of fineness.

It is used for uniting both brass and iron.

Copper-Tin Alloys.—Gunmetal and the bronzes.

Gunmetals.—The copper-tin alloys containing from 8 to 11 per cent. of tin are most suitable where a combination of strength, elasticity, toughness, and ability to withstand shock are required (Law).

The alloy containing 10 per cent. of tin has a tenacity of about 14·7 tons. It is used for many purposes in engineering, for parts of machines, etc., and for bearings; but for the latter, zinc, manganese, and other metals and phosphorus are generally added.

The mechanical properties of these alloys are markedly improved if phosphorus has been used as a deoxidizer in their manufacture (see "Phosphor-Bronze" below.)

Bell Metal.—Copper alloyed with from 15 to 25 per cent. of tin, the former being used for small and the latter for large bells.

Speculum Metal.—Copper 66·6 per cent., tin 33·4 per cent. Formerly used for reflectors, but now rarely made.

Phosphor-Bronze.—In the manufacture of the copper-tin alloys phosphorus is frequently added in small quantities in the form of phosphor-copper or phosphor-tin as a deoxidizer, and in excess to confer special properties on them. Of these alloys, bronzes containing less than 9 per cent. of tin and only traces of phosphorus are put on the market as "rolled or malleable phosphor-bronze," and can be used with advantage for all purposes for which copper and soft bronzes are suitable, such as condenser tubes, fire-box stays, bolts, etc.

"The phosphor-bronzes most commonly employed contain :—

"(1) 8 to 10 per cent. of tin, and 0·5 to 0·7 per cent. of phosphorus.
(2) 10 to 12 ,, ,, 0·7 to 1·0 ,, ,,
(3) 10 to 12 ,, ,, 1·0 to 1·5 ,, ,,

"The first of these is suitable for valves, pinions, pumps, propellers, steam fittings, etc. It is harder and wears better than gunmetal. The second alloy is considerably harder than the first, and is suitable for worms, worm-wheels, cylinders, motor gearing, etc. The third is an exceptionally hard alloy without being brittle, and is capable of withstanding the hardest wear. It is suitable for worm-gearing, slide valves, bearings, and all cases in which the wear is excessive" (Law).*

Arnold Philip † recommends the following specifications :—Copper 90 to 92 per cent., tin 7·4 to 9·7 per cent., "to give in large castings an ultimate tensile strength of over 17 tons per square inch and an elongation on 2 inches of not less than 20 per cent." Copper 91·5 to 97·5, phosphorus 0·10 to 0·25, tin the remainder, for rod, sheet, or wire. The tensile stress unannealed being over 30 tons per square inch, with an elongation of 10 per cent. on 2 inches.

"For turbine blades there is an old-fashioned alloy which has proved useful and in some instances decidedly preferable to steels because it is non-rusting.*

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* Law, *Alloys*, p. 157.

† Philip, "Notes on Phosphor Bronze," *Journ. Inst. Met.*, vol. i., pp. 166, 168.

" For this purpose only the pure copper-tin-phosphorus alloy is of value. The composition and general physical characters of this alloy is indicated by the following specification :—

" Tin not under	3 per cent.	nor over	5 per cent.	
Copper ,,	94·9 ,,	,,	96·9 ,,	
Phosphorus ,,	0·1 ,,			

The metal containing from 3·5 to 4·0 per cent. of tin is preferred.

" Maximum stress not under	24 tons per square inch.	
Elongation on 6 ins. ,,	10 per cent.	
,, 2 ins. ,,	13 ,,	

Aluminium Bronze.—This term is applied to several alloys of copper and aluminium containing from 4 to 10 per cent. of the latter metal. Those containing from about 6 to 7 per cent. have a high tenacity, about 28 to 29 tons per square inch. They can be readily forged and rolled, and drawn cold. See also p. 606.

Aluminium bronzes containing from 9 to 11 per cent. of aluminium have been found by Carpenter and Edwards † to be the most suitable alloys to withstand high hydraulic pressures. That containing 9·9 per cent. closely resembles Swedish-Bessemer rolled steel, containing about 0·35 per cent. of carbon, in physical and mechanical properties.

When manganese is added to aluminium bronzes the property of resisting abrasion to a remarkable extent is conferred on them, thus an alloy consisting of copper 88·11, aluminium 8·91, manganese 2·98 lost only 10·0 mgrms., whilst tool steel under the same conditions lost 27·4 mgms. (Rosenhain and Lantsberry).‡

Manganese Bronze.—The alloys sold commercially as manganese bronze are usually alloys of copper containing about 4 to 6 per cent. of manganese and alloys of copper and zinc to which ferro-manganese has been added. The chief characteristic of the former is their strength at comparatively high temperatures ; they have hence been adopted for fire-box stays.

When the alloys contain less than 9 per cent. of manganese they can be rolled and drawn. The alloys consisting of copper, zinc, and manganese should be termed manganese brasses. Many contain only traces of manganese, and others none at all. In these any properties they may possess is due to the deoxidizing action of the manganese and the presence of iron, of which they usually contain over 1 per cent. They are superior to ordinary brasses in mechanical properties and are used for the same purposes.

An important application of manganese bronze is in the manufacture of propellers, as such propellers are but little acted on by sea water.

" Parsons' manganese bronze," which is largely used for the blades of turbines and centrifugal pumps and other purposes where resistance to sea water or water carrying sand is required, has the following composition :—Copper 58·0, zinc 38·5, tin 1·0, aluminium 1·0, iron 1·0, manganese 0·5.*

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* Parker, *Journ. Inst. of Metals*, 1915, vol. xiv., p. 56.

† Eighth Report Alloys Research Committee, 1907.

‡ Ninth Report Alloys Research Committee, 1909.

Turbadium bronze,† which is used mostly for propeller castings, on account of its resistance to corrosion by sea water, has the following approximate composition :—

Cu,	48·00 per cent.
Zn,	46·45 ,,
Sn,	0·50 ,,
Pb,	0·10 ,,
Fe,	1·00 ,,
Al,	0·20 ,,
Mn,	1·75 ,,
Ni,	2·00 ,,

The tensile strength is 35 to 42 tons per square inch, with 14 to 20 per cent. elongation on 2 inches.

Copper-Nickel Alloys.—The chief alloys consisting only of copper and nickel are the following :—

	Cu.	Ni.
Coinage alloy,	75	25
Constantan wire for electrical resistance,	60	40
Driving bands of projectiles,	95	5

Nickel-Silver.—The most important and extensively used alloys, however, are those of the Cu-Zn-Ni series, the so-called "German silvers." They are very variable in composition, the common kinds sometimes containing not more than 7 per cent. of nickel.

According to Hiorns the composition of the following qualities of German silver made by the best makers in Birmingham in 1890 was as follows :—‡

	Cu.	Ni.	Zn.
Extra white metal,	50	30	20
White metal,	54	24	22
Best Best,	50	21	29
Seconds,	62	14	24
Fourths,	55	10	35

The following analyses of five specimens of commercial nickel-silver were made by Gadsby, of the Heeley Silver Mill, Sheffield, in 1915 :—§

Cu,	60·08	61·25	55·60	58·38	55·49
Zn,	28·31	27·42	31·43	22·37	20·66
Ni,	9·91	10·55	12·17	18·77	23·06
Fe,	0·81	0·35	0·32	0·25	0·35
Mn,	nil	trace	nil	trace	trace
Sn,	0·21	trace	trace	trace	trace
Pb,	0·77	0·38	0·41	0·21	0·25

In addition to those there are several intermediate qualities. Nickel-silvers can be rolled, drawn, or spun, and are largely used alone as a substitute for silver, and as the basis of electroplated ware and other articles.

Copper and Lead.—Copper forms no useful alloy with lead (see "Lead," p. 178).

Besides the alloys above mentioned there are several special bronzes containing other metals in addition to copper and tin. Of these the following are the most important :—

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* *Metallurgie*, 1908, p. 567.

† *Chem. News*, 1915, vol. cxii.

‡ Law, *Alloys*, 1st edition, p. 175.

§ *Journ. Inst. Met.*, vol. xv., 1916, p. 255.

	Cu.	Sn.	Zn.	Pb.
Metal for bearings,	86·0	12·0	2·0	...
Naval bronze,	88·0	10·0	2·0	...

	Cu.	Sn.	Zn.	Pb.
Ordinary axle-box bearings (*Hughes*),	80·0	5·0	...	15 0
British coinage alloy,	95·0	4·0	1·0	...

ORES OF COPPER.

There are many copper minerals, but few are found in sufficient abundance to be considered ores, and of these the chief, which may be divided into three groups, are as follows :—

1. Native copper. 2. Sulphide ores. 3. Oxidized ores.

1. **Native Copper.**—The most extensive deposits in the world are those of the Lake Superior region, where it occurs disseminated through amygdaloid and conglomerate lode matter, ranging in size from fine particles up to masses of several tons in weight. It is generally very pure and is the source of the noted "Lake" copper.

Native copper also occurs in small quantities in Yunnan in China, New Mexico, and Peru.

2. **Sulphide Ores.**—The most widely distributed and abundant of these ores is chalcopyrite.

Chalcopyrite, commonly called copper pyrites and yellow copper ore, is $CuFeS_2$.

When pure it contains 34·81 per cent. of copper. Iron pyrites, and in some cases magnetic iron pyrites, generally occur with it in considerable quantities, and these mixed ores are the chief sources of copper. They often contain not more than 1 per cent. of copper, yet even with this low percentage, as we shall see later, they can be worked with profit for the extraction of the metal. Gold and silver are often present in sufficient quantities to increase considerably the value of the ore to the smelter.

Chalcopyrite also occurs in small but payable amounts in the iron pyrites, notably in Spain, which is used in the manufacture of sulphuric acid.

In Japan it occurs intimately diffused in massive magnetic pyrites.

Copper Glance or Chalcocite, Cu_2S.—When pure it contains 79·79 per cent. of copper. It occurs extensively in the United States, and is the chief source of copper in the Butte district, also an important ore in Arizona, Utah, and Nevada. It is also found in Cornwall, Russia, and elsewhere.

Chalcocite is rarely pure, part of the copper being usually replaced by varying amounts of iron.

Bornite (Erubescite, Peacock ore).—A double sulphide of copper and iron extremely variable in composition, the copper ranging from 42 to 70 per cent. It is found in many localities, but not on a very extensive scale.

Enargite.—A mixed copper arsenic sulphide to which the formula $4CuS, Cu_2S, As_2S_3$ is usually assigned. It occurs in Montana and Peru, and is the source of the arsenic in Manilla copper.

Tetrahedrite (Fahl ore, grey copper ore).—A cuprous sulphide in which the copper is replaced more or less by iron, zinc, silver, and mercury, and is associated with variable proportions of antimony and arsenic sulphides. It always contains silver, sometimes being highly argentiferous as in the Harz, Clausthal, and Colorado, where it is treated for that metal. It is rarely worked for the copper alone on account of the arsenic and antimony which are present.

3. **Oxidized Ores.**—In this group, in addition to the true oxides, are included the carbonates and also the silicates.

They are the products of the decomposition of sulphide ores, and are usually found associated with iron oxide in the gossan or upper decomposed portion of mineral veins, which at lower depths yield sulphides only. They are of wide distribution, but only in a few localities do they occur on an extensive scale; hence they are less important as sources of copper than the sulphides from which they are derived.

Cuprite (red oxide of copper), Cu_2O, contains 88·8 per cent. of copper when pure. Although of wide distribution, it is found generally only in small quantities associated with other surface ores, and is of importance in but few localities. In Yunnan it occurs in lumps containing a core of native copper, and is there a valuable ore. It was once an important ore at Burra Burra and at one or two mines in the United States.

Melaconite (black oxide of copper), CuO, contains when pure 79·8 per cent. of copper. Melaconite often contains various amounts of iron and manganese oxides. A very impure form was formerly worked on a large scale in the Blue Ridge mines of Tennessee, North Carolina and Virginia.

Malachite (green carbonate of copper), $CuCO_3 + Cu(OH)_2$, contains 57·33 per cent. copper when pure. It is found in numerous localities, but not generally in large quantities. There are, however, large deposits in the Urals and Australia, and in the Tanganyika district, Africa, it is the chief ore. It frequently occurs merely as a thin coating of barren vein stuff to which it gives a fictitious appearance of richness.

Azurite (blue carbonate of copper), $2CuCO_3 + Cu(OH)_2$, contains 69·2 per cent. of copper when pure. It occurs along with other oxidized ores, but is nowhere abundant.

Chrysocolla.—A hydrated silicate of copper. When pure it is a bluish-green mineral containing about 40 per cent. of copper, but its composition is very variable from admixture with free silica, etc.

It occurs in the Urals in association with malachite and in Chili and Korea.

Atacamite, $CuCl_2 + 3Cu(OH)_2$, contains when pure 59·4 per cent. of copper. A hydrated copper oxychloride only found in abundance in Chili and other parts of the west coast of South America.

The "Porphyry" Ores (*so-called*).—These ores consist of finely divided chalcocite and chalcopyrite disseminated through prophyry and other rocks. They occur on a very extensive scale in Utah, Northern Nevada, Arizona, and New Mexico.

They are all low-grade ores containing only from 1·75 to 2·2 per cent. Cu with very small amounts of gold, 0·015 to 0·02 oz., and silver 0·3 to 1·0 oz. per ton. They can be easily and cheaply concentrated, and are the sources of very large amounts of copper.

In addition to the above ores an important ore in Germany is the *copper schist* (Kupferschiefer) of Mansfeld. It consists of a bituminous calcareous schist containing 2 to 3 per cent. of copper chiefly as pyrites disseminated through it, also small amounts of silver. It is largely smelted at Mansfeld after roasting.

THE EXTRACTION OF COPPER.

The extraction of copper from its ores is carried out by the following methods :—

1. Dry or smelting methods.
2. Wet methods.

By far the greater proportion, probably 90 per cent., of the total production of copper is obtained by smelting.

Wet methods are not in general use on a very large scale except at Rio Tinto. They are chiefly applied to poor ores in which the copper can be converted into sulphate or chloride, and from the solutions of those salts the metal is obtained by precipitation chiefly with iron, also by electrolysis.

The Principles of Copper Smelting.

Oxide Ores.—If the ores are " oxide ores," such as the copper carbonates, cuprite, etc., the operation of smelting is simple. They have only to be charged into a blast furnace with coke or charcoal together with suitable fluxes, if these are necessary, when on smelting, so-called " black copper " containing 97 to 98 per cent or more of copper will be produced, but the slags will be much richer than those obtained on smelting sulphide ores, and will frequently contain as much as 2 per cent. of copper. Hence whenever it is possible pyritic ores should be obtained for smelting with them.

Sulphide or Pyritic Ores.—When the ores are sulphide ores the operations are more or less complicated, but the slags are cleaner and contain less than 0·5 per cent. of copper.

The operations are based on—

1. The greater affinity of copper than iron for sulphur.
2. The greater affinity of iron than copper for oxygen.
3. The reactions with which iron oxide combines with silica to form a fusible slag.
4. The property possessed by copper sulphide of mixing perfectly with iron sulphide and also with other sulphides to form mattes.
5. The higher specific gravity of mattes compared with those of suitable slags.
6. The property possessed by copper mattes of dissolving the gold and silver in auriferous and argentiferous ores, and thus extracting them.

It will be evident from the above that part of the sulphur and iron in a pyritic ore must be oxidized, but sufficient sulphur must be left unoxidized to combine with the copper and some of the iron to form a matte of the required composition, and sufficient silica must be present to combine with the iron oxide formed to produce a fusible ferrous silicate slag. The copper in a 2 to 10 per cent. ore will then on smelting be concentrated into a matte containing 20 to 40 per cent., while the FeO and other bases in the gangue will combine with the SiO_2 to form a slag.

The oxidation of the sulphur may be effected by two methods, viz. :—

1. *By roasting.* 2. *By pyritic smelting.*

The matte and slag whilst in a state of fusion separate readily, owing to the difference in their specific gravities, the slag floating on the heavier matte.

The percentage of copper in the matte will depend on the percentage of sulphur left unoxidized. There must, however, be sufficient sulphur left unoxidized to combine with some of the iron as well as with the copper to form a Cu-Fe matte, otherwise there will be a loss of copper in the slag.

The process is hence a concentration process by which the copper in the ore is concentrated in a matte.

Further, if the operations of roasting followed by smelting with silica be applied to the matte it is evident that more of the iron will be removed and the matte will become sufficiently rich in copper for the direct extraction of the metal.

In modern practice, however, in all the most important works, with only one or two exceptions, the matte first obtained is sufficiently rich to be converted into copper by the process of Bessemerizing.

Before proceeding further it will be convenient to consider here the nature and constitution of the mattes produced by smelting.

Copper Mattes.—In addition to the iron sulphide which is always present, copper mattes may also contain sulphides of nickel, lead, silver, zinc, etc., as well as arsenides and antimonides. Their constitution has been the subject of many investigations, but it has not yet been definitely settled. The results of some investigators may be briefly summarized as follows :—

Hofman, Caypless, and Harrington, from their researches,* have come to the conclusion that Cu_2S and FeS do not form any definite combinations, but that a eutectic exists containing 85 per cent. FeS and 15 per cent. Cu_2S which melts at 850° C.

A diagram showing the freezing-point curve of copper-iron mattes worked out by these investigations is reproduced in Fig. 25.

C. B. Carpenter and C. R. Haywood † consider that cuprous and iron sulphides are completely soluble in each other when liquid, but are only partly soluble when solid, the two branches of the liquidus curve intersecting at a eutectic point corresponding to 32 per cent. cuprous sulphide. The eutectic range extends from 50 per cent. to 7·5 per cent. cuprous sulphide.

According to F. H. Edwards ‡, the copper sulphide-iron sulphide system forms a series of solid solutions, with the two branches of the melting point curve meeting at a minimum of 940° C. at a composition of 36 per cent. cuprous sulphide, no trace of a eutectic being present.

The important property possessed by mattes of dissolving gold and silver has been pointed out above.

In this connection the action of the following constituents of Cu-Fe mattes should be noted.

Cuprous sulphide readily dissolves and collects silver and gold.

Metallic copper, a common constituent of copper mattes, also dissolves silver and gold.

Lead sulphide dissolves silver sulphide, but has little action on gold.

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* *Trans. Amer. Inst. of Min. Eng.*, 1907.

† *Eng. and Min. Journ. Press*, 1923, vol. cxvi., p. 453.

‡ *Trans. Inst. Min. and Met.*, 1924, vol. xxxiii., p. 492.

Zinc sulphide has but little action on either silver sulphide or on gold.

Iron sulphide is practically without solvent action on silver sulphide or gold.

Metallic iron, a common constituent of mattes, is not a good solvent of silver, but readily dissolves gold.

Hence the constituents of mattes, which are chiefly of value as collectors of the precious metals, are Cu_2S and Cu and in a lesser degree Fe and PbS.

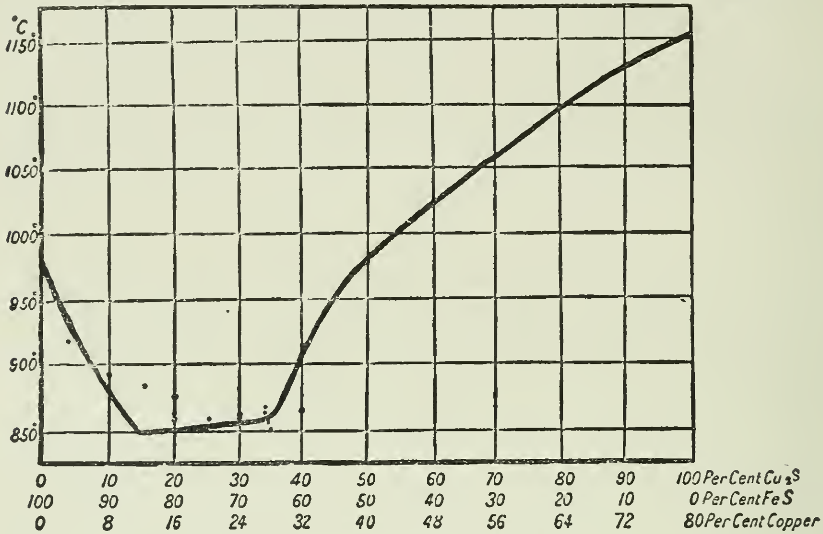

Fig. 25.—Freezing-Point Curve of Mattes.*

The property possessed by mattes of dissolving gold and silver enables copper ores containing even less than 2 per cent. of copper to be smelted with profit, and during recent years considerable amounts of the precious metals have been thus extracted.

The Processes of Copper Smelting.

The methods of extracting copper from its ores by smelting may be divided into the following classes :—

I. *Smelting Sulphide Ores in Reverberatory Furnaces.*
    (*a*) After previously roasting.
    (*b*) Without previous roasting, but with the addition of oxidized ores or cupriferous materials.
    (*c*) Smelting roasted fines or concentrates.
II. *Smelting Sulphide Ores in Blast Furnaces.*
    (*a*) After previous roasting part of the ore.
    (*b*) Smelting raw sulphide ores (pyritic or partial smelting).
III. *Smelting Oxide Ores in Blast Furnaces.*

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* Levy, *Modern Copper Smelting*, p. 38.

Roasting.—Since the introduction of pyritic and partial pyritic smelting, the roasting of copper sulphide ores has been largely given up, and the sulphur contained in them is now utilized as fuel in the blast furnace.

Formerly the percentage of copper in an ore was an important factor in deciding whether it should be roasted or not, but now the character of the ore is of the chief importance, thus, for example, a pyritic ore with only about 2 per cent. of copper as in Tennessee and suitable for pyritic or partial pyritic smelting is not roasted, whilst an ore consisting of copper glance (chalcocite), enargyrite, and a little pyrites containing about 5 per cent. of copper, but with a large amount of quartz and aluminous gangue as in Butte, is roasted after being first concentrated to about 10 per cent. of copper.

The process is, in fact, chiefly confined to the treatment of pyritic concentrates and screenings or fines from lump ore. The former usually ranges in size from $\frac{1}{4}$ inch downwards. The latter consists of material which will pass through a $\frac{1}{2}$-inch mesh sieve, and is too small for charging into the blast furnace.

The chief object of roasting pyritic copper ores is, as already pointed out (p. 68), to remove so much of the sulphur by oxidation by means of heat and air that the remainder, when the roasted ore is smelted, may be sufficient to combine with the whole of the copper and with so much of the iron that a matte of the mixed sulphides containing the desired percentage of copper may be obtained, and much of the iron be removed as ferrous silicate. Therefore complete roasting is not necessary, and generally the operation is only carried out until about 5, 6, or 8 per cent. of sulphur is left in the ore, so that the required grade of converter matte may be obtained in the reverberatories on smelting.

The roasting may be effected in two ways :—

(*a*) By ordinary roasting processes. In these the material remains in pieces of the same size as before roasting, and if in fine particles is only suitable for smelting in reverberatory furnaces and not in blast furnaces unless it is briquetted, which is not always satisfactory.

(*b*) By "blast" roasting in which the particles of ore are agglomerated and obtained in lumps suitable for smelting in the blast furnace.

The reactions and changes which occur in roasting a pyritic copper ore may be briefly stated as follows :—

Equation 1. $FeS_2 = FeS + S$.
,, 2. $FeS + 3O = FeO + SO_2$.
,, 3. $2FeO + O = Fe_2O_3$.
,, 4. $3FeO + O = Fe_3O_4$.
,, 5. $3FeS + 11O = Fe_2O_3 + FeSO_4 + 2SO_2$.
,, 6. $2FeSO_4 + O = Fe_2S_2O_9$.
,, 6*a*. $Fe_2S_2O_9 = 2SO_3 + Fe_2O_3$.
,, 7. $SO_2 + O = SO_3$.
,, 8. $CuS + 3O = CuO + SO_2$.
,, 9. $Cu_2S + 4O = 2CuO + SO_2$.
,, 10. $2CuS + 7O = CuO + CuSO_4 + SO_2$.
,, 10*a*. $CuO + SO_3 = CuSO_4$.
,, 11. $CuSO_4 = CuO + SO_3$.

1. Any iron pyrites present first loses part, not quite an atom, of its sulphur, as free sulphur which burns in blue jets on the surface of the ore forming SO_2, the FeS_2 becoming nearly FeS.

2, 3, 4, 5. The FeS is oxidized, Fe_2O_3, Fe_3O_4, and $FeSO_4$ being formed.

6. $FeSO_4$ is decomposed by heat and oxygen into basic ferric sulphate.

6*a*. Basic ferric sulphate is decomposed into $SO_3 + Fe_2O_3$ at about 600° C.

7. By far the greater part of the SO_2 is evolved as such, but a small amount is converted in the presence of oxygen and the highly heated ore and walls of the furnace into SO_3.

8, 9, 10, 10*a*. Copper sulphides are oxidized similarly to iron sulphide, $CuSO_4$ is also formed by the action of the SO_3 from the decomposition of $FeSO_4$, on CuO.

11. At a higher temperature than $FeSO_4$, about 850° C., $CuSO_4$ is decomposed, but usually some remains unaltered in the roasted product.

Pyrrhotite behaves in a similar manner to pyrites.

The roasted ore will finally consist of copper and iron oxides with more or less copper sulphates and unaltered iron and copper sulphides. If galena or zinc blende are present in the ore they will be converted into oxides and sulphates.

When arsenic and antimony sulphides are present, part of the arsenic and of the antimony are oxidized respectively to As_4O_6 and Sb_4O_6, which are volatilized and at the same time SO_2 is given off. Part, however, is oxidized further with the formation of arsenates and antimonates, which are not decomposed at the temperature of the roasting furnace and will remain in the roasted product.

Roasting of Lump Ore.—If lump ores have to be roasted, either heap roasting (p. 19) or stall roasting (p. 22) may be employed. The cost of the two processes does not differ much, and in windy and wet districts the latter has great advantages over the former, especially so, as the stalls can be covered with a roof and loss of copper due to washing out of the sulphate by rain is prevented. Both processes are, however, becoming obsolete. At Rio Tinto, where oxidation in heaps is carried out on a very extensive scale, the operation is a unique one, and has for its object the formation of copper sulphate which is leached out from the heaps by special arrangements (p. 161).

At Mansfeld, Germany, where the copper bearing shale (Kupferschiefer) contains about 13 per cent. of bituminous matter, heap roasting is necessary. The heaps are 130 feet long, 7 feet high, 16 feet wide across the top, and 24 feet across the bottom. A heap is kindled with brush wood placed round its base, and when combustion is once started the ore is self-burning.

Ores consisting of iron pyrites containing from 1 to 2 or 3 per cent. of copper are roasted in England and elsewhere in kilns at sulphuric acid works, the SO_2 evolved being utilized in the manufacture of the acid. The roasted product is termed "burnt ore," and is either smelted with sulphide ores as described (p. 79), or is treated by a wet process (p. 158) for the extraction of the copper.

Ordinary Roasting of Fines and Concentrates.—For this operation many forms of roasting furnaces are in use, but modern practice in America has decided in favour of the MacDougall *type* of roaster. At the Washoe plant of the Anaconda Company, where roasting is carried out on a scale of great magnitude, Brückner cylinders were given up some years ago and were replaced by MacDougall furnaces, as modified by Evans and Klepetko (see pp. 34 and 35). Similar furnaces have been erected at Tooele (Utah), at Garfield (Utah), at Steptoe (Nevada), and at many other works. The advantages possessed by this furnace are low cost of labour and small consumption of fuel.

At Anaconda crushed limestone in sufficient quantity to act as a flux and produce the slag required in the reverberatory furnaces is charged along with the fines and concentrates into the roasters.

A modification of the MacDougall furnaces by Herreshoff in which the rabbles are cooled by air instead of by water has been erected at the new plants of the Calumet and Arizona Company (Douglas) and the Arizona Copper Company (Clifton).

The hand-worked four-hearth reverberatory is nearly obsolete. It has been given up at practically all copper works and been replaced by mechanically worked furnaces.

The Brückner cylinder (p. 39), the White and White-Howell (p. 40), and other revolving horizontal cylinders are being superseded by mechanically rabbled furnaces, and are not being erected at the latest new plants.

The most important of the other old furnaces which are is use are—

1. The Brown straight line (p. 25).
2. ,, Wethey (p. 27).
3. The Ropp straight line (p. 29).
4. ,, Pearce turret (p. 33).

The roasted products from all these furnaces are only suitable for smelting in reverberatory furnaces, as they are in too small particles for the blast furnace. The roasting furnaces may be placed so as to discharge into bins above the reverberatory furnaces in order to conserve heat. Roasting plants are sometimes equipped with Cottrell installations to recover dust (see p. 108).

Blast Roasting.—Blast roasting, which is in extensive use for the treatment of lead ore, has not proved so successful with copper ores, and in some cases where it has been tried has later been abandoned. It has been in successful use at the Ashio smelter of the Furukawa Mining Co., Japan, and at Wallaroo, South Australia.

At Wallaroo the M'Murtry-Rogers process was successfully used. This process may be taken as typical of several desulphurizing and sintering processes applied to the treatment of copper ores. It resembles the Huntington-Heberlein process for galena, but lime is not used, and it is conducted as follows :—*

The pots used are of cast iron, and take a charge of 8 to 9 tons of wet ore. They are mounted on trunnions, are 8 feet 8 inches in diameter inside, and 4 feet 6 inches in depth, with steep sides. A false bottom, slightly convex, perforated with $\frac{5}{8}$-inch holes, is placed about 10 inches above the lowest part of the pots. A blast pipe 8 inches in diameter enters at the back of the pot below the false bottom. The pressure of blast is 13 ozs., and the volume of air is about 1,000 cubic feet per minute.

The charge must contain silica or siliceous material amounting from 15 to 35 per cent. of silica and from 15 to 25 per cent. of sulphur. The ore

* Cloud, *Trans. Inst. Min. Met.*, vol. xvi., p. 311, *et seq.*

must be well wetted, and unless the water is in excess ferric oxide is formed around the particles and their agglomeration prevented.

The charges which burn best consist of, roughly, one-third of pieces about 1-inch to $1\frac{1}{4}$-inch gauge and two-thirds of fine ore from jigs and other dressing appliances.

The process consists in first covering the false bottom with pieces of a previously burnt charge broken up, from 3 to 4 inches in size, then lighting a small fire in the middle of the pot on the top of this material, using a light blast to urge on the fire. Part of the charge is then introduced until the pot is about half full. After increasing the blast to 13 ozs. until the ore has become more or less red in several places the remainder of the charge is added until the pot is full.

The blowing is continued until the evolution of sulphur dioxide slackens and the charge has become red-hot throughout. The blast is then stopped, the blast pipe disconnected, the pot inverted, and the cake of sintered material allowed to fall on four or five cast-iron cones by which it is more or less broken up. The time required for working a charge varies from eight to twelve hours. The sulphur in an ore containing 10 to 12 per cent. of copper and 20 per cent. of sulphur is reduced to about 5 to 6 per cent.

The advantages claimed for the process are that the losses of fine material as dust in the ordinary roasting operations are avoided and the product is in a form admirably adapted for blast-furnace smelting.

At the Copperhill plant of the Tennessee Copper Co., the Dwight-Lloyd straight-line machine, described under "Lead" (p. 198), has been used, and also at one or two other works. In present practice, however, blast roasting is not in favour, and at most of the important copper works one or other of the furnaces just mentioned are employed for roasting, and the products are smelted in reverberatory furnaces.

The chief disadvantage of the blast-roasting process is the frequent imperfect sintering of a considerable proportion of the charge.

Reverberatory Furnace Smelting.

Reverberatory furnaces are specially suitable for the smelting of ore fines and of concentrate, which have been previously roasted, and are now extensively used owing to the development of flotation processes, as it is found to be cheaper to make a tailing of the gangue than to make a slag of it.

During recent years they have undergone many important changes, the old small furnaces have been given up, and at all important works there has been a marked increase in their size. In Montana in 1903 there were several with hearths 50 by 20 feet, but since then at the Washoe plant of the Anaconda Company, Mathewson has erected several of extraordinary size with hearths measuring not less than 116 feet in length by 16 feet in breadth, and several of larger dimensions have been constructed at other works (see also pp. 85 and 93).

With every increase in size there has been a great reduction in the consumption of fuel and in other working expenses. Further, with the largest furnaces one of the serious disadvantages of reverberatory smelting—*i.e.*, the intermittent character of the work—has been materially lessened and the process has become practically a continuous one analogous to that of blast furnaces, there being no stoppage of the furnace for charging after tapping.

Economy in fuel is further effected in the large reverberatories by raising steam with the waste heat of the furnace gases by fitting Stirling and other boilers in connection with the flues, and by the use of oil and powdered coal.

In the new Noranda Smelter, the reverberatory furnaces have no waste-heat boilers, but are fitted with a recuperative system.

The efficiency of the reverberatory furnace has also been greatly increased in the large furnaces at Anaconda (Fig. 32), Copper Cliff, and Garfield, by feeding and fettling along the side walls and abolishing the side doors.

Owing to the success which has been attained by the use of oil and powdered coal as fuel (see p. 90), the reverberatory furnace has again taken a foremost place in copper smelting, and in many large plants blast furnace smelting has been given up, although the furnaces are kept in reserve to be used in emergencies.

The flotation process for ore concentration, too, which has now come into extensive use, is also in favour of the reverberatory furnace, as the concentrates obtained in this process are in a very fine state of division, an unsuitable form for blast-furnace smelting.

A reverberatory furnace, however, must be worked at its full capacity to ensure extreme economy, and it may be remarked further, that it must be of large dimensions to compete with the blast furnace. It follows, therefore, that the blast furnace will not be completely displaced by the reverberatory from the smelting field. In many small plants it will still be found to be the best furnace for reducing their ores, and even in the largest works employing reverberatories, there will be times and conditions when the blast furnace can be utilized with advantage.

As regards the relative efficiency of these large reverberatory furnaces and blast furnaces, no definite pronouncement that will be universally applicable is possible.

" Each kind of furnace is admirable in its own way and is incompetent for others " (Peters). The features in which each excel may be briefly stated as follows :—

1. The reverberatory furnace does not require power like the blast furnace, whilst it can supply steam power from its waste heat as mentioned below.

The blast furnace, however, is more suited to high silica slags and for highly pyritic ores, which can be treated by pyritic smelting, it has no equal.

2. The cost of fire-brick, refractory materials, and repairs is greater in reverberatory than in blast-furnace practice, but, on the other hand, inferior kinds of coal, also oil, can be employed as fuel.

The capacity of the largest reverberatories is 600 tons and upwards per day with coal-dust firing, and is practically equal to that of an ordinary blast furnace, but when the supply of ores is not uniform in character the blast furnace is superior to the reverberatory.

There is not necessarily a very great difference between the cost of smelting in the reverberatory and in the blast furnace, but this, of course, depends on the nature of the ore available and on local conditions.

It is, however, only in exceptional cases that the reverberatory furnace can be employed with efficiency and economy in ore smelting, except for concentrate and " fines."

In many places reverberatory copper-matting furnaces using pulverized coal as fuel can be operated more cheaply than blast furnaces, even where the coke consumption in the blast furnaces is as low as 8 per cent.

According to E. P. Mathewson,* "The essentials for successful reverberatory practice to-day are much as they have been in the past—namely, self-fluxing ores, cheap fuel, and cheap silica-bricks—whereas for blast-furnace practice the charge may be more refractory, but must be either sintered or nodulized or come naturally in lumps, and in addition the fuel and the power must be comparatively cheap.

"The exit of the blast furnace is not yet in sight, but owing to the great increase in tonnage treated by oil-flotation and the improvements in reverberatory practice, the reverberatory has been gaining materially in tonnage treated."

Blast furnaces must be preferred for ores, the gangues of which carry gold and silver values, and for ores containing oxidised compounds of copper with the sulphide.

Until comparatively recent times the most important process of copper smelting was the Welsh process. It was conducted in reverberatory furnaces and consisted of at least six distinct operations, but often seven or eight were required. It is now obsolete, at least as far as its six operations are concerned, but it illustrates so well the principles on which the extraction of copper from its ores by smelting is effected, that it will be described in outline.

Various modifications of the process have been introduced from time to time in which several of the operations are omitted and the process itself much shortened, but the reactions and principles on which they depend are the same.

The Welsh Process of Copper Smelting.

The problem to be solved is the extraction of copper from copper pyrites mixed with iron pyrites in a quartz gangue by the joint agency of air and heat.

The ore usually treated contained from 8 to 10 per cent. of copper as determined by the dry assay. The smallest number of operations or stages was six, but it was only when there was a suitable supply of oxidized ores that they were reduced to that number. The operations were as follows :—

1. *Roasting the Ore.*—Termed "calcination" by the Welsh smelters, the fifth operation only being called "roasting."

2. *First Fusion.*—The "calcined" ore was melted with slags from No. 4. The products were—matte called "coarse metal," and slag called "*ore furnace slag*," which should be poor enough to throw away.

3. "*Calcination*" *of the coarse metal.*

4. *Second Fusion.*—The "calcined" coarse metal was melted with slags from operations Nos. 5 and 6, and oxidized ores when obtainable.

The products were—a regulus, which is more or less pure cuprous sulphide called "white metal," and slag called "sharp" slag, which goes to No. 2.

5. *Roasting and Melting the White Metal.*—Carried out in a smelting

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* *Mining and Scientific Press,* Sept. 1919.

reverberatory furnace producing crude copper called "blister copper," and slag called "roaster" slag rich in copper, which goes to No. 4 operation.

6. *Refining the Blister Copper.*—Producing "tough" or "refined" copper and refinery slag very rich in copper, which goes to No. 4 operation.

1. "*Calcination.*"—This was always carried out in a reverberatory furnace with a bed measuring about 20 to 30 feet in length and 10 to 12 feet in breadth.

The "calcination" was only a partial one, as enough sulphur must be left in the ore to combine with the whole of the copper and some of the iron, so that when the "calcined" ore was melted a matte, consisting on an average of 34 per cent. of copper, 34 per cent. of iron, and the remainder chiefly sulphur with small amounts of impurities, would be obtained.

This was the composition aimed at, but there was in practice considerable variation in the percentages, both of copper and iron and also of sulphur.

2. *First Fusion.*—Termed "running for coarse metal." This was carried out in a reverberatory furnace called the "ore" furnace with, formerly, a small bed only about 13 feet 6 inches in length and 9 feet 6 inches in breadth and a bottom of siliceous sand. The "calcined" ore was melted with "sharp" slag containing 2 to 4 per cent. of copper from the fourth operation, the charge of ore being about 1 ton. When melted it was well stirred, and, after being allowed to settle for a time, the slag was skimmed off through the front door into sand moulds.

Another charge of "calcined" ore and slag was now put in and melted, stirred, and skimmed as before; the coarse metal was then tapped out through a taphole in the side of the furnace.

The slag was practically ferrous silicate, $FeSiO_3$, mixed with silicates of the earthy bases and alumina present, and usually contained not more than 0·5 per cent. of copper, which was diffused through it as small globules or shots of coarse metal. This slag was thrown away except the middle pig, which had usually to be put into the furnace with the next charge.

The ferric oxide in the "calcined" ore is converted by the unoxidized ferrous sulphide into ferrous oxide, which combines with the silica to form fusible ferrous silicate, $FeSiO_3$.

$$3Fe_2O_3 + FeS = 7FeO + SO_2.$$
$$FeO + SiO_2 = FeSiO_3.$$

Part of the silica combines with earthy bases which may be present forming silicates, which together with the ferrous silicate form a slag.

The whole of the copper combines with sulphur to form Cu_2S, owing to the great affinity of copper for sulphur. The remaining sulphur combines with part of the iron to form FeS.

The Cu_2S and FeS unite when molten to form the coarse metal.

The copper has thus been concentrated from 8 to 10 to about 34 per cent., and the gangue of the ore has been got rid of.

3. "*Calcination*" *of the* "*Coarse Metal.*"—The coarse metal, after granulating or grinding was usually "calcined" in a reverberatory furnace. In some works a Gerstenhöfer furnace was employed and the sulphur dioxide was utilized for the manufacture of sulphuric acid. The object of this "calcination" was, further, to oxidize the copper, iron, and sulphur, so that

when the roasted coarse metal was melted in the next operation more iron might be got rid of as silicate in the slag.

4. *Second Fusion.*—" Running for metal," the term " metal " not meaning metallic copper, but a regulus of cuprous sulphide or approaching thereto. The furnace was practically the same as the ore furnace.

The charge consisted of about 2½ tons of " calcined " coarse metal with varying proportions of slags from the fifth and sixth operations, both of which are rich in cuprous oxide and copper silicate, and oxidized ores. When the charge had been well melted and skimmed the regulus was tapped out into sand moulds. The regulus should be white metal, Cu_2S, almost free from iron, but generally it contained only 70 to 75 per cent. of copper. When, however, sufficient oxidized ores were not available a regulus called " blue " metal, containing only about 55 to 60 per cent. of copper, was produced and an extra operation was required for its treatment. The slag called " metal " slag or " sharp " slag was practically a silicate of iron and contained from 2 to 4 per cent. of copper.

Reactions.—The iron sulphide, on melting the " calcined " coarse metal, reacts with the copper silicates and cuprous oxide present in the " roaster " and " refinery " slags, giving rise to the formation of cuprous sulphide and ferrous silicate.

$$Cu_2O + FeS = Cu_2S + FeO.$$
$$2Cu_2SiO_3 + 2FeS = 2FeSiO_3 + 2Cu_2S.$$

The silica required to combine with the iron oxide was derived from the slags and ores, and some also from the furnace bottom and lining.

5. *Roasting to Blister Copper.*—The pigs of white metal, about 3, 4, or more tons, were charged into a furnace of precisely the same kind as that used for the second and fourth operations with this exception that it had a port hole or opening on each side of the fire-bridge, also one or more openings in the roof over the fire-bridge for the admission of air. The white metal in lumps was piled up high and, as much as possible, near the fire-bridge. The fire was regulated so that it melted slowly and trickled down in drops in order to expose it thoroughly to the oxidizing action of the air, all the air holes being open.

When melted the slag was skimmed off to expose the surface of the metal to the action of the air in order that further oxidation might take place. When the surface was again covered with slag it was again skimmed and these skimmings and oxidations were repeated several times.

After each skimming the charge was allowed to cool a little in order that it might " work " or " boil " when SO_2 was vigorously given off. During this stage the regulus was in violent agitation from the escape of the SO_2. When the charge had ceased working, the whole of the regulus, if the operation has been properly conducted, will have been converted into " blister copper." The temperature of the furnace was then increased, the slag skimmed off, and the blister copper tapped into sand moulds. The time required was about twenty-four hours, but it varied greatly according to the amount of iron and other impurities present.

The blister copper was so-called from the blisters produced on its upper surface by the escape of SO_2 during solidification.

The slag termed " roaster " slag was a copper-iron silicate, the last skimmings containing also Cu_2O and shots of copper. The percentage of copper in the slags varied greatly from the beginning to the end of the charge, the last slags containing up to 35 per cent. They were sent to the fourth operation.

The reactions were—

$$\begin{aligned} Cu_2S + 3O &= Cu_2O + SO_2. \\ Cu_2S + 2Cu_2O &= 6Cu + SO_2. \end{aligned}$$

6. *Refining.*—This operation was carried out in small furnaces, the charge being usually only about 6 to 8 tons. It was conducted in exactly the same manner as described on p. 140.

Various modifications of the old Welsh process have been introduced into works with a view to diminishing the number of operations and to economize time and labour.

In some works where the ores smelted are not very pyritic and where oxidized cupriferous materials are sometimes available, or burnt cupriferous pyrites can always be obtained from sulphuric acid works, "calcination" is dispensed with, and the ore charge is smelted at once in reverberatory furnaces.

During recent years some of these works have adopted the blast furnace for smelting the ore to matte, although they still employ the reverberatory furnace for subsequent operations.

The operations in the most common modification of the Welsh process are given in the diagram, Fig. 26.

The procedure is as follows :—

1. *Smelting for Coarse Metal.*—The furnaces are generally not very large, the hearths being usually 22 to 24 feet long and 14 to 16 feet broad, with a fire-box about 4 feet 6 inches by 5 feet and 4 feet 6 inches deep.

The charge consisting of raw ore, burnt pyrites, and slags from No. 2 is either thrown in through the side door or dropped in through one or more hoppers.

The total weight of the charge is about 16 tons, and is divided into four lots of 4 tons each.

After the first lot is charged, the furnace doors are closed and luted and the fire urged. When melted it is well stirred and allowed to stand for about an hour to allow the matte to settle ; the slag is then skimmed from off the matte into sand moulds as in the old Welsh process, but the matte is not tapped. A second lot of the smelting mixture is then charged in and treated in the same way. The third and fourth lots are similarly dealt with, and the matte is then tapped into sand or iron moulds. The matte will usually contain about 30 to 35 per cent. Cu and the slags 0·25 to 0·75 per cent.

The reactions are the same as in the Welsh process, but the concentration is here effected by the Fe_2O_3 in the burnt ore acting on the FeS in the raw ore in the presence of SiO_2 as follows :—

$$FeS + 3Fe_2O_3 + 7SiO_2 = 7FeSiO_3 + SO_2,$$

the iron going into the slag.

The Fe_2O_3 is reduced by the S in the FeS to FeO, which then combines with the SiO_2.

Smelting for White Metal.—The coarse metal is not "calcined," but is

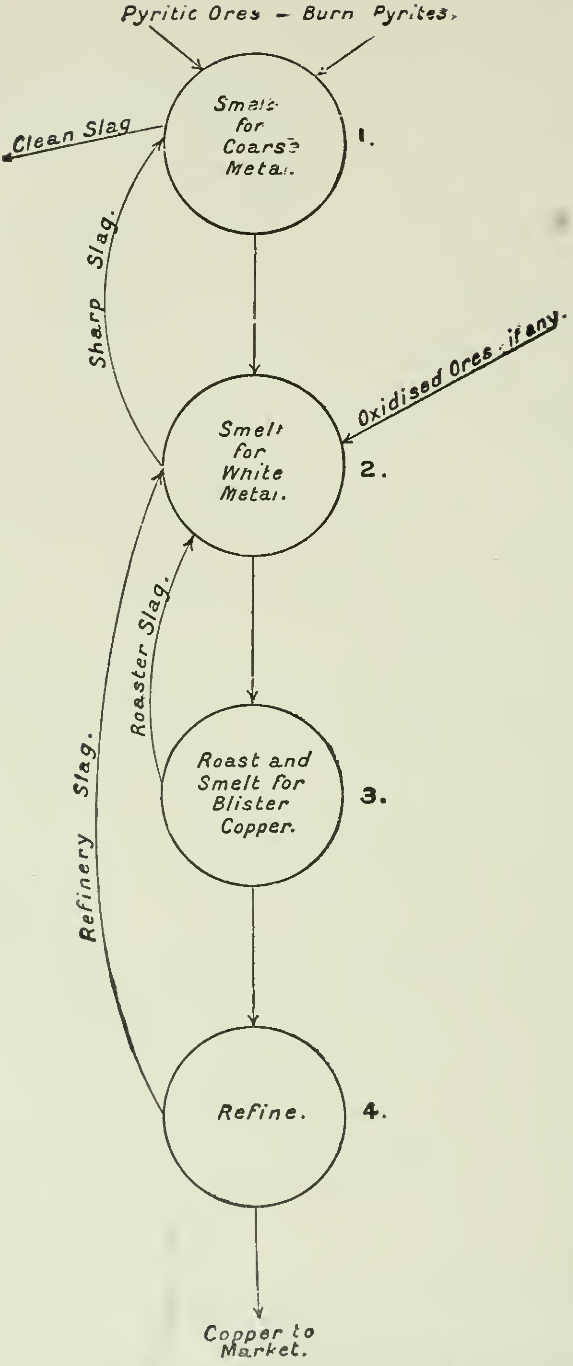

Pyritic Ores – Burn Pyrites.
Clean Slag
Smelt for Coarse Metal.
1.
Sharp Slag.
Oxidised Ores – if any.
Smelt for White Metal.
2.
Roaster Slag.
Refinery Slag.
Roast and Smelt for Blister Copper.
3.
Refine.
4.
Copper to Market.

Fig. 26.—Flow Sheet. Modification of the Welsh Process of Copper Smelting.

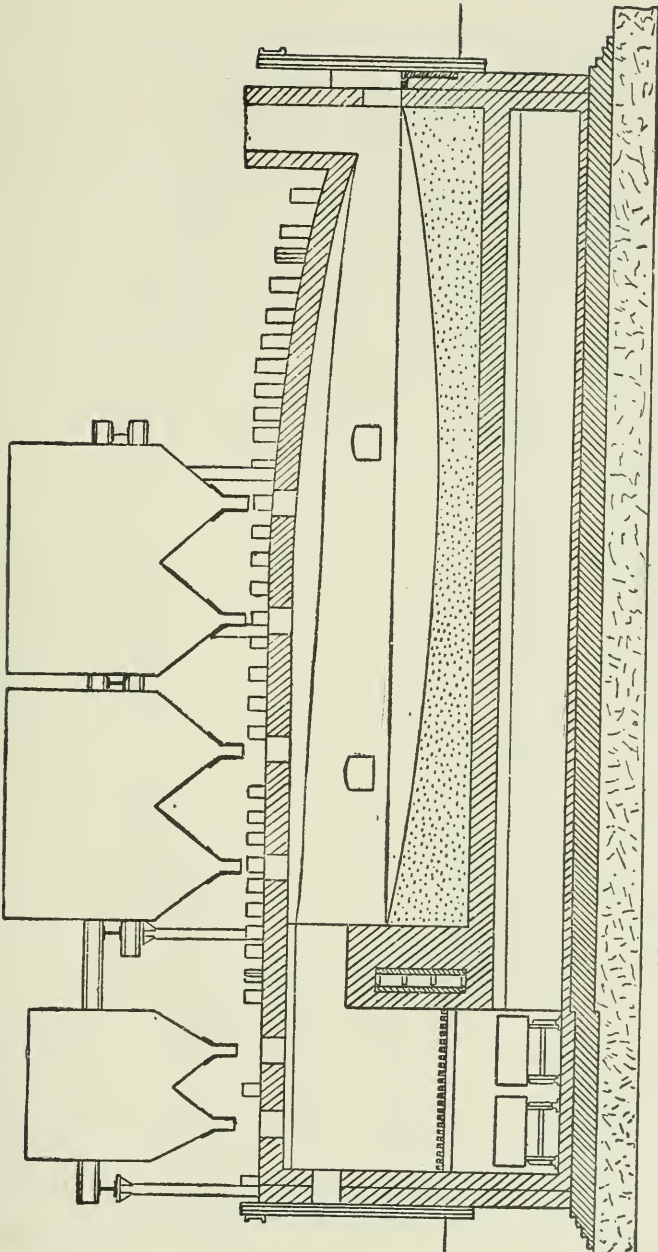
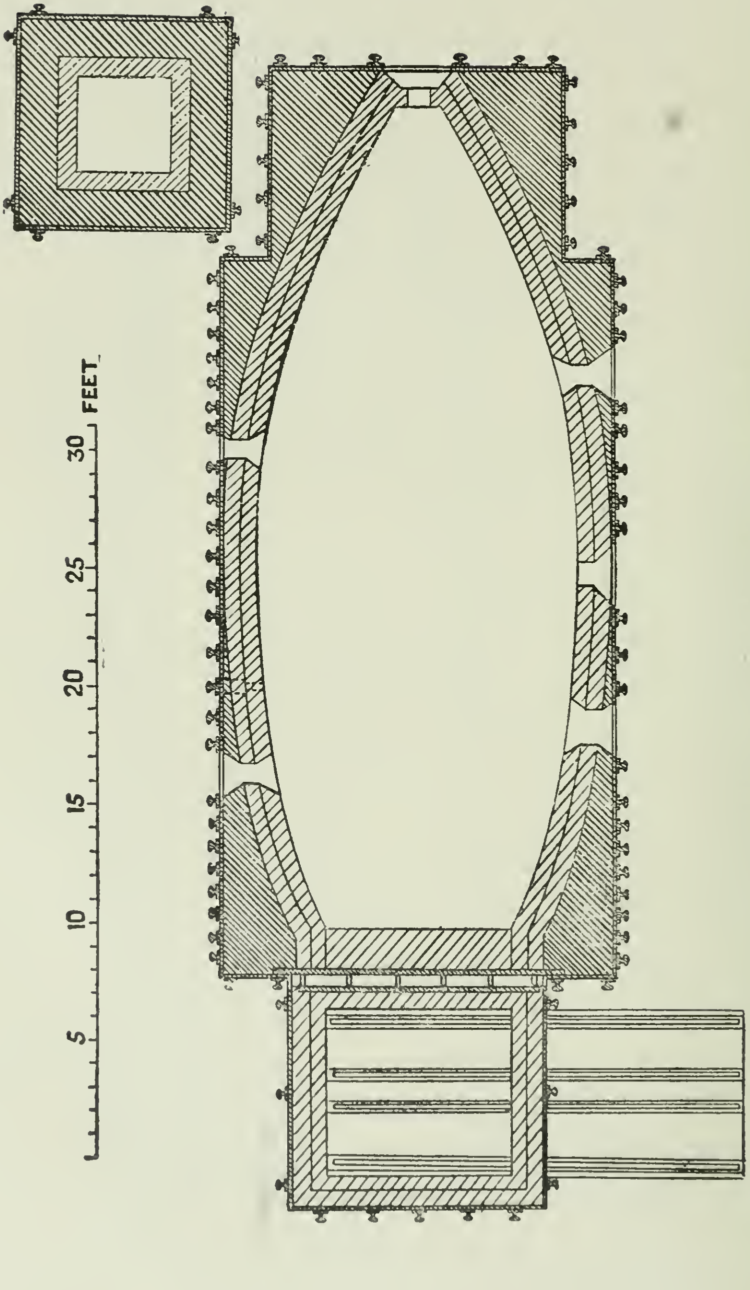


Fig. 27.—Reverberatory Furnace for Smelting Copper Ores—Section.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30
25
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15
10
5

Fig. 28.—Reverberatory Furnace for Smelting Copper Ores—**Plan.**

smelted with oxidized materials and slags from the roaster and refining furnaces as in the Welsh process.

The operation without "calcination" of the coarse metal can only be successfully carried out in works where copper refining is carried on on a sufficiently large scale to furnish a suitable supply of cupriferous slag, as oxidized ores are rarely available in sufficient quantity. It is also attended with a serious disadvantage—viz., the introduction into the white metal of the impurities in the refinery slag.

The process is conducted in a similar manner to the preceding operation, the furnace and charge being the same, 12 to 16 tons, and the latter being divided into four lots, but the white metal is tapped out after each two lots have been melted and the slag skimmed into a slag bogie.

Roasting for Blister Copper.—This operation is conducted as in the old Welsh process, but in larger furnaces.

Refining.—This operation is carried on as described on p. 140.

In almost all the most important works where reverberatory smelting is practised the smelting furnaces are generally of large size with hearths ranging from 50 by 20 feet to 116 by 19 feet, but there are many smaller works where a reverberatory furnace may be used with advantage for fines, concentrate, etc., at which the supply of these materials is insufficient to keep a large furnace employed. A suitable furnace is shown in Figs. 27 and 28.

The foundation in America frequently consists of a bed of slag from 2 to 4 feet in thickness, which is run whilst molten into an excavation prepared for it corresponding to the size of the furnace.

Upon this several courses of fire-brick are laid to complete the foundation, and upon this structure the walls and fire-bridge of the furnace are built and the hearth or working bottom is constructed.

At some works a bed of concrete is put in instead of a bed of slag. In England the furnaces are usually built on vaults which run the entire length of the hearth.

On the sill plate at the front of the furnace a series of two or three thick wrought-iron plates are laid and kept in position by projections from the door jambs. The number depends on the height to which the slag may be expected to rise above the sill plate. The top of the uppermost one should carry a dam of ganister, which, when opened, will allow the slag to run out, raking being dispensed with.

The chief dimensions of the furnace are—Hearth 36 feet long and 15 feet wide at the middle; fire-box 8 feet long by 6 feet wide, the fire-bars being 3 feet or 3 feet 6 inches below the top of the fire-bridge, according to the character of the coal.

The fire-box should have a lining of 9-inch Stourbridge or similar bricks and an outer wall of common fire-bricks or of red brick. In some works silica bricks are used for the lining. There should be an opening in the back wall of the fire-box, through which the fire-side of the fire-bridge can be repaired or fettled. This is kept closed by bricks luted in, except when required. Below the fire-box is the ash pit about 5 feet 6 inches in depth for "grating"—*i.e.*, clearing the bars of ash and clinker. The conker plates are of cast iron, one to afford support to the lining of the fire-box and a heavier one to strengthen the fire-bridge. Between them is a 6-inch air space for cooling the fire-bridge

Width of fire-bridge, 3 feet 6 inches.
Height of roof above fire-bridge, 2 feet.
" " hearth at flue, 2 feet.

The roof should be of 12- or 14-inch hard-burnt silica bricks and the sides of the same, the latter having a backing of 9-inch common silica or red brick. There are two doors on each side of the hearth for the purposes of rabbling the charge and fettling the furnace, and one on one side or in some cases on both sides for skimming off the slag. The door in front of the furnace is the chief skimming door.

There are four openings in the roof over which iron hoppers are fitted for introducing the charges, and two similarly fitted in the roof of the fire-box for feeding in the fuel The buckstays are best made of I beams set together in groups with horizontal bars near their upper extremities pierced to take the tie rods. The lower extremities of each group are best held in position by an iron plate, against which is built a brick wall, or against which a bed of slag has been run in whilst molten.

Capacity about 50 to 70 tons in twenty-four hours. If provided with its own chimney stack, this should be about 4 feet 6 inches in internal diameter and 80 feet in height.

The hearth or bed is sometimes made of two courses of 9- or 12-inch silica brick, but is generally, in fact nearly always, of sand, ground quartzite, or ganister. In the latter case the siliceous material should contain about 95 per cent. of silica.

If not in the form of sand, it should be ground to pass through a $\frac{1}{4}$-inch sieve. The furnace having been thoroughly dried and heated to redness about 5 or 6 tons of the sand or ganister is charged in and heated for about five or six hours with frequent rabbling. Another lot is then charged and treated in the same way. This operation is repeated until sufficient sand to form the bottom, which should be from 18 to 20 inches or more in thickness, is in the furnace. After the whole has been thoroughly calcined the temperature of the furnace is raised until the sand begins to frit. The bed is then formed by spreading the sand carefully in the shape required and beating it down with long iron tools with shallow spoon-like heads.

The openings of the furnace are then luted up and the temperature raised as high as possible and kept up for twelve or sixteen hours. After being allowed to cool slowly down to full redness, a mixture of slag and ore is thrown over the bed and melted down. Small charges are then worked for three or four days, the furnace being allowed to cool down to redness between each. The furnace is then ready for regular work.

At some works the bottom of refining furnaces is put in in two layers, the lower being laid and fired on before the sand for the upper is treated, but for ore smelting it is usually a single layer.

The furnace is worked as follows :—

The charge of roasted ore about 15 tons, preferably hot from the roasting furnaces, is fed in through the hoppers, also any cupriferous materials or slags. The charge falls upon a bath of molten matte which has been left in the furnace. over which it spreads, being assisted with rabbles by the workmen through the side doors. At some works, in order to avoid loss by dusting and too great a cooling of the furnace, a door in the chimney stack is opened by which the rush of cold air over the hearth is diminished.

When the charge is all in the doors are luted up, and after two or three hours the furnaceman with a rabble rakes off the bottom any ore which may by chance have adhered to the hearth, but this is unusual. In five or six hours from the time of charging, the charge should be perfectly melted and ready for skimming. This is effected by removing part of the fire-clay dam, and the iron plate in front of it at the front door, and allowing the slag to run out into a slag pot on wheels, whilst slag is also similarly removed at the side door or doors and by skimming. Any matte which may pass out with the slag will collect at the bottom of the slag pot and may be recovered.

The matte is not tapped until about 20 tons have accumulated in the furnace, the taphole is then opened and the matte run out into iron moulds, leaving about 5 or 6 tons in the furnace.

After several charges have been smelted the sides and fire-bridge will be more or less deeply cut away and corroded chiefly at the slag line, and will require to be fettled. This is accomplished with moistened ganister, or with ground quartz made into a stiff paste with fire-clay, so that it may be made into large balls which are placed in the corroded parts with long spoon-like tools and well tamped in.

Reverberatory Smelting of Fines and Concentrate in Large Furnaces.—In the United States and at Cananea, Mexico, reverberatory furnaces of extraordinarily large size are in use at several works for smelting fines, concentrate, and flue dust, where there is an abundant supply of ore.

The most important are those given in the following table (see also p. 93) :—

EXAMPLES OF REVERBERATORY FURNACES IN AMERICA, 1912.*

Locality.	Number.	Dimensions of Hearth.		Dimensions of Fire-box.	Average Boiler H.P. per Furnace from Waste Heat.	Average Tonnage per Day.
		Length.	Breadth.			
Anaconda, Montana, .	8	111′ 8″	19′	7′ × 16′	560 H.P.	253
Cananea, Mexico,	2	100′	19′	oil-fired.	971 H.P.	192·3
Garfield, Utah. .	6	112′	19′	7′ × 18′	330 H.P.	240
Steptoe, Nevada,	5	120′ 10″	19′	8′ × 19′	486 H.P.	239
,, ,,	5	120′ 10″	19′	oil-fired.	632 H.P.	322
Tooele, Utah, .	5	102′	19′	7′ × 16′	390 H.P.	325
Clifton, Arizona (1915), . .	3	100′	22′	oil-fired.	1660 H.P.	365

* Taken from Table by E. P. Mathewson, *Min. and Sc. Press*, 9th November, 1912.

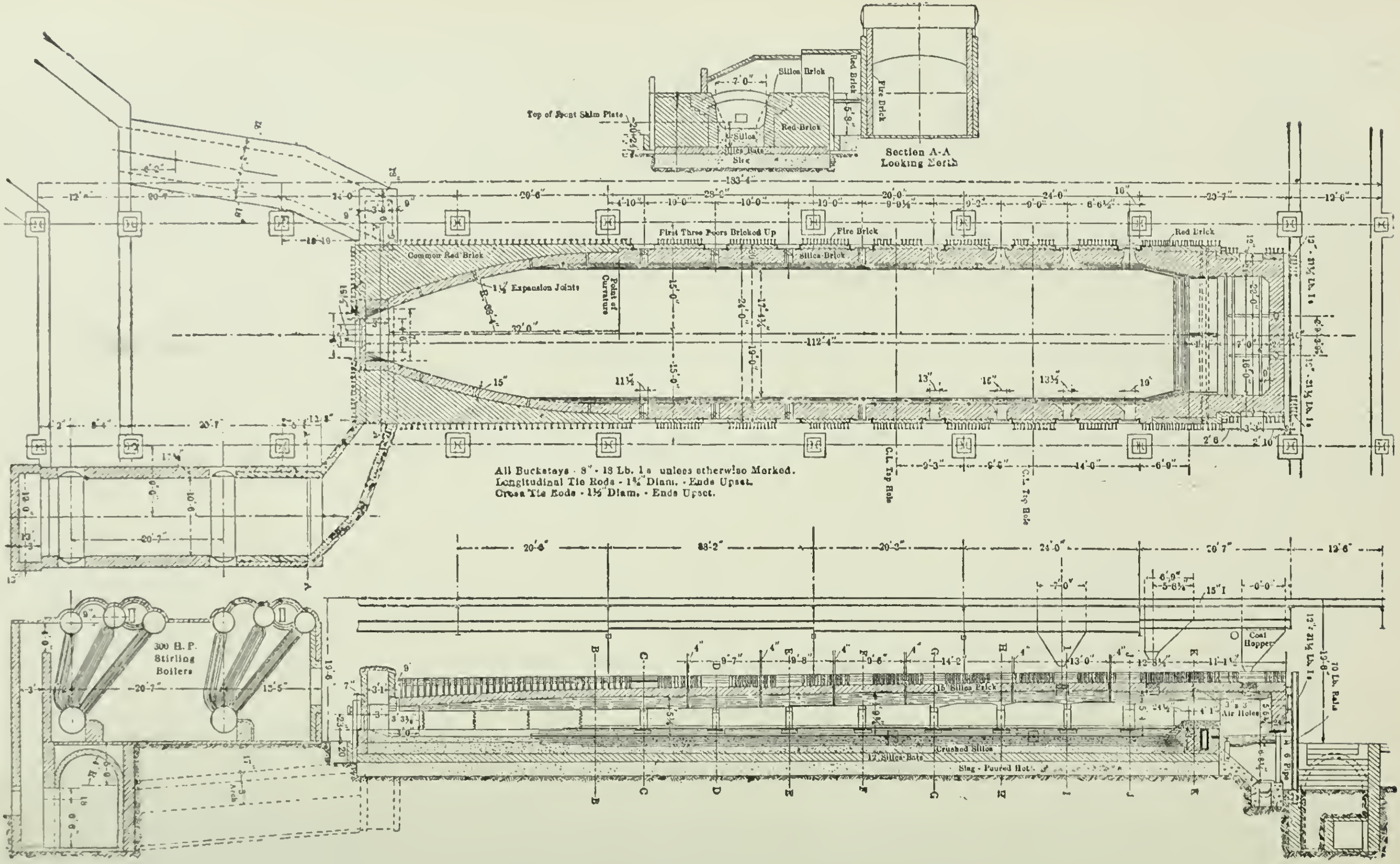
Section A-A
Looking North
Top of Front Skim Plate
Silica Brick
Red Brick
Fire Brick
Silica
Silica Bote
Slag
Common Red Brick
First Three Doors Bricked Up
Silica Brick
Red Brick
1¼" Expansion Joints
Point of Curvature
112'-4"
183'-4"
C.L. Tap Hole
C.L. Tap Hole
All Bucksteys · 8" · 18 Lb. I s unless otherwise Marked.
Longitudinal Tie Rods · 1¾" Diam. · Ends Upset.
Cross Tie Rods · 1½" Diam. · Ends Upset.
300 H. P.
Stirling
Boilers
Coal
Hopper
70 Lb. Rails
12" 31½ Lb. I s
15" I
16" Silica Brick
3" x 3" Air Holes
6" Pipe
Crushed Silica
12" Silica Bote
Slag · Poured Hot
Arch
A
B
C
D
E
F
G
H
I
J
K

Fig. 29.—Old Reverberatory Furnace at Washoe.

The large furnaces which were first erected at the Washoe plant of the Anaconda Company, as stated on p. 74, on account of their success, have been adopted as a standard elsewhere. The furnaces at the works mentioned in the table are of similar design and construction, and are worked in a similar manner.

A sectional plan and elevation of one of the furnaces at Washoe are shown in Fig. 29.*

For the alterations made in 1915 in the dimensions and mode of working the furnaces at Washoe, see pp. 93-94.

The dimensions of the hearth and fire-box are given in the table. The ratio of hearth to grate area is 16 : 1.

The fire-bridge is 4 feet across, and is 27 inches above the hearth and 2 to 3 feet above the fire-bars.

The height from the hearth to the crown of the arch is 6 feet 7 inches near the fire-bridge and 4 feet at the front.

The walls are 26 inches and the roof 15 inches thick, except over the fire-box and fire-bridge, where its thickness is 20 inches.

All parts of the furnace exposed to the action of the charge and heat are of silica brick except the bottom, which is of sand containing 97·5 per cent. of silica.

The method of working at the Washoe plant until firing with powdered coal was adopted (1915), p. 93, was as follows :—

There were eight furnaces, seven being usually at work and one under repair.

An important feature in working these furnaces was that a layer of matte from 4 to 13 inches in thickness was constantly kept in the furnace to protect the hearth.

The furnace was charged about every sixty-five or seventy minutes.

The charge was dropped from the hoppers within 20 feet of the fire-bridge, 10 tons from the first and 5 tons from the second. As soon as a charge had fused, a fresh one was dropped. The bulk of the material charged was hot "calcines" (roasted material) from the MacDougall roasting furnaces. The charge fell on a layer of at least 4 inches of matte and about 8 inches of slag, consequently, it did not reach the bottom, and hence sticking of the charge to the hearth was avoided. The hot charge spread out over the surface of the molten materials and floated towards the front of the furnace, usually disappearing when half-way down.

Every four hours the furnace was skimmed through the front door, the slag being allowed to flow through a cutting in a sand dam built within the door.

The slag passed into a cast-iron slag pot to catch any matte it might contain, and overflowing was granulated by a stream of water and washed away.

The matte was tapped when required by the converters into iron ladles lined with a mixture of siliceous ore and slime from the settling ponds. The tapholes were situated between the second and third and between the fourth and fifth doors.

Coal was charged every forty minutes in quantities of 1½ tons at a time from a hopper through four holes in the roof of the fire-box.

The fire was clinkered or grated about every four hours. A good deal

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* Offerhaus, *Eng. Min. Journ.*, June, 1908, pp. 1189 and 1234.

ANALYSIS OF MATERIALS USED AND PRODUCED IN THE ABOVE FURNACES.*

Locality.		Cu.	Ag.	Au.	SiO_2.	Fe and Mn.	CaO.	S.	Al_2O_3.
		Per cent.	Ozs. Per ton.	Ozs. Per ton.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Charge.	Anaconda,	9·31	6·43	0·028	28·63	26·46	3·50	7·34	5·22
	Cananea,	6·43	2·22	0·14	26·96	31·34	2·58	9·59	5·54
	Garfield,	12·00	3·50	0·16	30·00	22·50	11·50	10·50	4·50
	Steptoe,	13·60	0·401	0·078	26·80	25·90	5·80	9·50	5·30
	,, oil fired,	13·10	0·345	0·078	27·60	24·10	5·40	9·30	6·90
	Tooele,	2·90	3·80	0·11	30·50	35·00	3·80	6·50	..
Slag.	Anaconda,	0·39	0·19	0·0006	39·68	32·83	4·62	0·91	7·03
	Cananea,	0·35	0·11	..	37·44	33·58	3·83	1·08	7·96
	Garfield,	0·45†	0·08	trace	46·50	20·58	17·50	1·00	5·50
	Steptoe,	0·45†	0·06	0·005	40·20	28·90	10·50	0·40	7·60
	,, oil fired,	0·50†	0·02	0·007	42·00	25·90	10·90	0·20	8·00
	Tooele,	0·43†	0·45	0·008	40·50	36·93	4·00	..	..
Matte.	Anaconda,	41·68	28·40	0·130	0·27	26·54	..	25·76	..
	Cananea,	31·91	11·34	0·07	0·54	37·17	..	26·87	..
	Garfield,	42·00	10·00	0·50	..	27·00	..	26·00	..
	Steptoe,	41·76	1·25	0·25	0·70	29·00	..	25·10	..
	,, oil fired,	42·90	0·91	0·22	0·50	29·10	..	24·80	..
	Tooele,	23·00	27·50	0·85	0·50	43·00	..	26·50	..

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* Mathewson, *op. cit.*

† Converter slag is poured into the reverberatories at these plants; thus raising the percentage of copper.

of small and partially burned coal fell through the fire-bars, especially when clinkering, this was carried by a stream of water over a grizzly to separate the larger clinkers, and then to a jigging plant, where it was recovered. By this means 10 per cent. of the fuel charged into the furnace was reclaimed and went to the briquetting plant, where it was used as a constituent of the briquettes charged into the blast furnace.

A further economy of fuel is still effected by utilizing the heat of the furnace gases for raising steam. To that end, Stirling boilers are fitted in the flues as shown in Fig. 29.

An important innovation introduced at Anaconda was the regulation of the working of the furnace by the pressures of the draught. The pressures were registered automatically by water manometers, one of which communicated with the furnace over the fire-bridge and the other with the downtake flues. As the composition of the charges and the nature of the fuel were practically constant, it was found in practice that with a draught pressure of 0·85 inch at the fire-bridge and from 1·7 to 2 inches in the flue, the working of the furnace was at its best. The firing and clinkering could thus be regulated. From 250 to 325 tons of charge was smelted daily in each furnace with a consumption of from 55 to 60 tons of coal, 10 per cent. of the coal was, however, recovered in the cinders as coke.

At Cananea oil has replaced coal as fuel with a reduction in the costs of smelting. Less than one barrel is consumed per dry ton of charge, and of this quantity 0·43 barrel is chargeable to the raising of steam in the boilers.

Oil-firing has also been adopted at the Copper Queen, Steptoe Valley, Clifton, and several other works.

The advantages of these large furnaces are—

1. Continuous working. The serious losses of heat and time in the smaller furnaces where the entire melted charge is taken out and a new charge put in is thus avoided.
2. The consumption of fuel and the amount of labour required are greatly diminished.
3. The furnace bottom is preserved by the pool of matte which always remains in the furnace.
4. The charges are melted with great rapidity, the heat of the molten slag and matte being utilized for the heating of the fresh additions.
5. The use of the furnace gases for raising steam.

The special advantages of the use of reverberatories in conjunction with blast furnaces are concisely stated by Ricketts of Cananea as follows:—"They not only permit us to smelt our flue dust and fine concentrate for less than the ton costs in the blast furnace for the average mixture, but by removing fine material from the charge it lessens the blast-furnace ton costs in several obvious ways and decreases the flue dust losses." *

At Garfield, where the ore is carefully screened and nothing less than ⅜-inch pieces are sent to the blast furnaces, the remainder goes to the reverberatories. The result being that much less flue dust is formed in the blast furnaces than formerly, and a furnace 4 feet by 20 feet at the tuyeres puts through from 350 to 600 tons of charge per day, a rate per square foot of hearth area which exceeds that at any similar plant elsewhere.†

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* *Trans. Inst. Min. Met.*, 1910, vol. xix., p. 165.

† *Min. Mag.*, vol. i., p. 322.

Alterations in the Furnaces and Method of Working them at Anaconda.—The adoption of the flotation process of concentration, to which the whole of the ore at Anaconda is now subjected, and the introduction at the same time of the use of powdered coal as fuel in the reverberatory furnaces, has revolutionized the smelting process at Washoe and Great Falls. A similar result has also followed at several important works.

Here it may be remarked that at Anaconda by this use of flotation it is expected to raise the percentage of recovery of copper from the ore from 78 to 91 per cent.

Before dealing with the changes in the smelting procedure, it will be convenient to consider first the mode of application of powdered coal as fuel.

Powdered Coal as Fuel in Copper Reverberatory Furnaces.—An advance of far-reaching importance in reverberatory furnace smelting is the recent introduction of the use of powdered coal for fuel. When powdered coal in suspension is mixed with air in the proper proportions and blown into a combustion chamber, it will burn with a flame similar in many respects to that of crude oil, and the flame is as easy to manage as gas. The combustion is more perfect than when the coal is of larger size, and there is no cooling of the furnaces by intermittent charges of fresh fuel in the fire-box.

Since 1895 it has been in use in firing cement kilns, and some years ago it was tried at the Highland Boy Works in Utah, and later by Shelby at Cananea, its use, however, at the two latter works was not continued, although the fuel economy resulting was clearly shown. At Cananea the ash of the powdered coal gave considerable trouble, choked up the throat, and unburnt coke blanketed the slag in the furnace.

In 1911 a reverberatory furnace 112 feet by 19 feet was started at the Canadian Copper Co.'s plant, Copper Cliff, Ontario, by Mr. D. H. Brown, and was a success from the beginning. As a result of this success, several large copper smelting works are now using powdered coal in their reverberatories, the output of each furnace being increased and the consumption of fuel diminished.

An enormous installation has been made at Anaconda, and equipments of somewhat less importance at Great Falls, Montana, and Garfield, Utah.

The nature of the coal that can be successfully used ranges between somewhat wide limits. The composition of the ash is important; it should not be so fusible that it will form accretions in the flues or in the tubes of the boilers placed within them, otherwise any good or even moderately poor coal may be used. According to E. P. Mathewson,* "coals varying in ash from 5 to 23 per cent. have been used successfully in pulverized form. Two points are essential for success. The coal must be dried below 1 per cent. moisture before pulverization, and the pulverization must be carried to a very fine point. Preferably, not over 5 per cent. of the pulverized coal should rest on a 100-mesh screen, while 95 per cent. should pass through a 100-mesh screen; not over 20 per cent. should rest on a 200-mesh screen, while 75 per cent. should pass through a 200-mesh screen."

The coal should if possible have a high volatile content, not less than 30 per cent., although some coal containing only 20 per cent. has been used. The use of culm or slack which is liable to contain much ash and pyrites is not always possible.

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* Internat. Engineering Congress, 1915, San Francisco, *Eng. and Min. Journ.*, Nov. 1915.

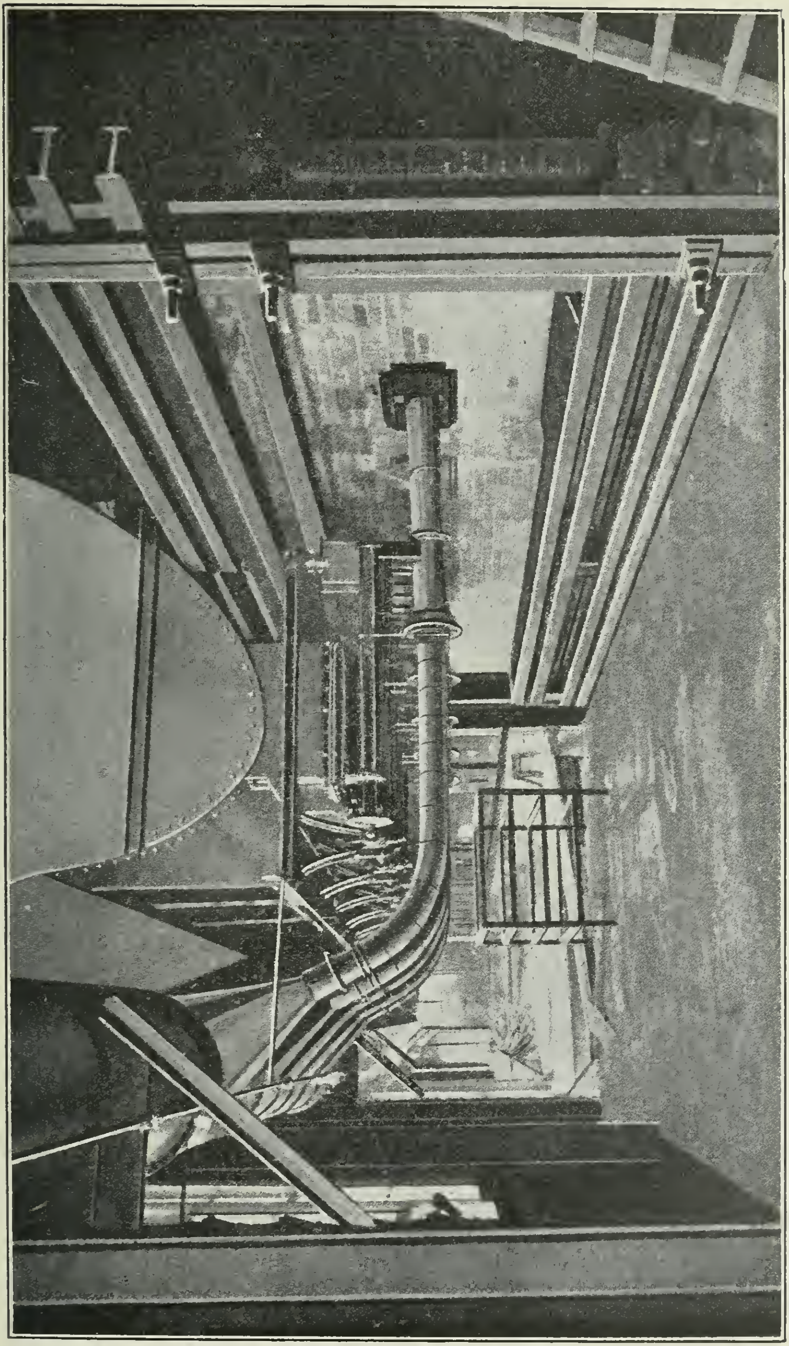

Fig 30.—Anaconda New Furnace, Firing End showing Warford Coal-Dust Burners.

The most modern plant for the pulverization of coal to be used as fuel in firing reverberatory furnaces is that erected by Mr. E. P. Mathewson at the Washoe Reduction Works, Anaconda. The description which follows is abstracted from an account by him in the *Engineering and Mining Journal*, of July 10th, 1915.

The coal is crushed to pass through a 2-inch mesh screen, it then passes over a magnetic pulley, which removes all scrap iron, nails, etc., and discharges it into revolving driers. From the driers it passes to disintegrators, in which it is reduced to ¼-inch size. It is then pulverized in five roller pulverizers, so that 96 per cent. of it will pass through a 100-mesh screen. An exhaust fan, placed above each mill, draws the coal from the mill as fast as it is reduced to the required fineness, and discharges it into a cyclone collector, where it is separated from the air. From the collectors the powdered coal is delivered by screw conveyors in air-tight housings to a 50-ton storage hopper at the firing end of each reverberatory furnace. From this hopper the coal is fed into the furnace by five Warford coal burners, one of which is shown in Fig. 31. In this burner the coal dust is carried forward by the screw to the end of the conveyer-housing, where it is discharged into four receiving pipes through a long slot; and what does not pass through the slot drops through a larger opening at the end upon the nozzle in the mixing chamber. The dust entering the mixing chamber is drawn to the end of the blast-nozzle, and thence into the furnace through 5-inch pipes, which in turn discharge into 8-inch pipes. The space between the 5-inch and the 8-inch pipes allows for secondary air to be drawn in as required to obtain complete combustion of the coal. The feed of coal and the primary and secondary air are under absolute control. All the machinery through which the coal passes is made dust-proof, so that but little dust is seen in the department. The blast pressure varies from 8 to 16 ozs. per

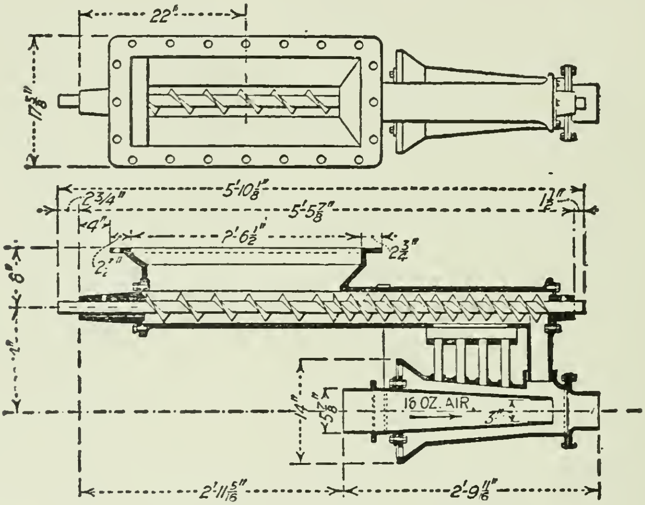

Fig. 31.—Warford Coal-Dust Feeder.

square inch. The arrangement of the burners and blast pipes at the firing end of a furnace is shown in Fig. 30, and needs no explanation.

At all plants using powdered coal as fuel the furnaces are of the large modern type. Their chief dimensions are given in the following table :—*

	Length.	Breadth.	Maximum Height of Arch above skim-plate.	
			Firing End.	Flue End.
Copper Cliff, Ontario, .	112′ 0″	19′ 0″	6′ 8″	4′ 8″
Anaconda, Montana, .	143′ 2″	23′ 4″	7′ 6″	4′ 6″
Garfield, Utah, . .	112′ 0″	19′ 0″	..	..
Great Falls, Montana, .	128′ 0″	22′ 0″	8′ 6″	4′ 10″

The capacity of these furnaces is from 400 to 700 tons, according to size.

At Anaconda, Montana, where all the difficulties hitherto met with, especially those arising from the ash of the coal, have been successfully overcome, the following installation has been made :—

The old reverberatory plant contained eight furnaces, Nos. 1-8, and another, No. 9, at the end of the converter buildings. Furnace No. 8 was the first one altered to coal dust firing being lengthened to 124 feet. Nos. 1-7 have been altered to approximately 144 feet long by 23 feet wide ; No. 7, of which the dimensions are given in the table above, is typical of the new furnaces. It is illustrated in Fig. 32.† The matte tap is at the front, 3 feet 2 inches to the left of the centre line, and 24 inches above it ; at 2 feet 9 inches to the right is the dam-plate of the slag tap.

At the firing end are five coal-dust burners. The method of feeding the charge to the furnace was changed at the same time that firing with powdered coal was adopted. Previously the charge was fed through holes about the centre line of the roof. The furnace is now charged along the sides by means of the hoppers and 10-inch charge pipes shown in the figure. The charge is fed in in small quantities at a time at frequent intervals, so that the walls are but little exposed to the heat. By this method of feeding the walls are protected, and a more uniform temperature is maintained in the furnace. In these furnaces there are no side doors, any fettling that may be required being dropped in through the feeding hoppers at the sides ; these are hence continued to the tapping end.

The slag is allowed to run off continuously, and any unfused floating material that may come down to the front of the furnace is fluxed by small additions of limestone.

At Anaconda the adoption of continuous over-flow of the slag from the reverberatory furnaces is said to have resulted in a decrease in the reverberatory slag loss. Each furnace smelts on an average 550 tons of charge for 24 hours, which will mean a slag production of about 369 tons. It is this large quantity, of course, that makes a continuous flow possible.

The door formerly used for skimming is bricked up, except for a suitable slot through which the slag escapes. The slag flows into a launder, which discharges it over the granulating jet. For a couple of feet outside the skimmings door, the launder is kept covered by a few large lumps of coal and one or two brick slabs, with fettling thrown on top. Over the remainder of the launder a crust of slag soon forms, the molten slag flowing under this crust. The percentage of copper in the slag was reduced from 0·41 to 0·35. This decrease of 0·06 per cent. of copper in the slag means an annual saving of 565 tons of copper.*

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* Kuzell, *Eng. and Min. Journ.*, Feb. 1916. (Paper presented at Second Pan American Congress, Washington, D.C.)

† Austin, *Min. and Scientific Press*, Feb. 1916.

The economy resulting from the use of these furnaces fired with powdered coal is well shown by the following record :—

The total charge smelted in one of the new furnaces in 24 hours was 676·3 tons, the charge being made up of 579·8 tons of calcined ore and 96·5 tons of flue dust. The total powdered coal used was 103·4 tons, the ratio of the coal to the charge being as 1 to 6·54, equivalent to 15·3 per cent., whereas the old furnaces, 115 feet long, previous to alteration smelted less than 300 tons with a coal consumption of 24·1 per cent. when worked with natural draught and ordinary coal firing.†

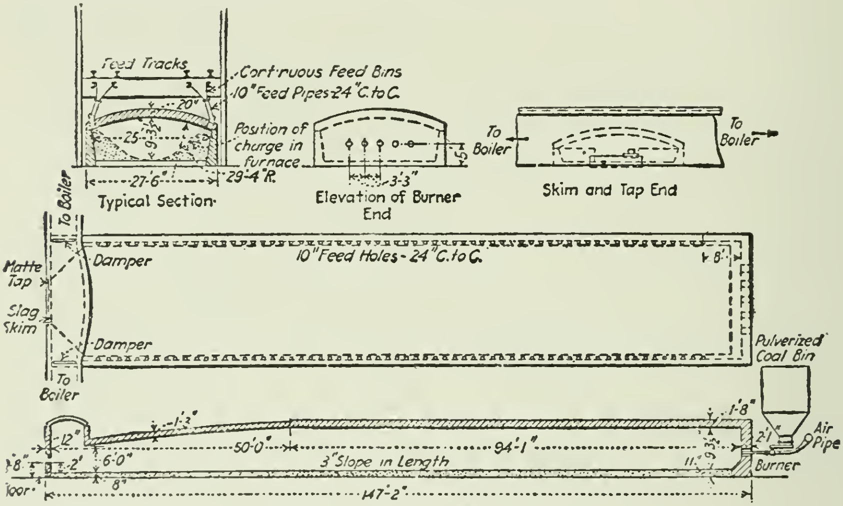
Feed Tracks
Continuous Feed Bins
10" Feed Pipes 24" C. to C.
20"
25'
9'-3½"
Position of charge in furnace
27'-6"
29'-4" R.
Typical Section
3'-3"
5'
Elevation of Burner End
To Boiler
To Boiler
Skim and Tap End
To Boiler
Matte Tap
Damper
10" Feed Holes - 24" C. to C.
8'
Slag Skim
Damper
To Boiler
Pulverized Coal Bin
1'-3"
1'-8"
12"
50'-0"
94'-1"
9'-3½"
2'-1"
Air Pipe
8"
2'
6'-0"
3" Slope in Length
11"
Burner
8"
Door
147'-2"

Fig. 32.—Anaconda New Furnace.

Smelting in Blast Furnaces.—For certain copper ores the blast furnace possesses advantages when compared with the ordinary reverberatory furnace, the chief of which are large output, economy in fuel, utilization in raw sulphide smelting of the sulphur as a source of heat, greater power of concentration permitting the treatment of low-grade ores, low smelting costs, and greater elasticity in working when the ores to be smelted are liable to vary in composition.

Its chief disadvantages are that fine ores or concentrate must first be either briquetted or sintered, or they can be smelted only when they form a small proportion of the charge.

The relative advantages of the two types of furnace have already been considered on p. 75.

Generally speaking, the best practice is to smelt the lump ore in blast furnaces and the fines and concentrate in reverberatory furnaces, and this procedure is followed in all important works.

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* Oliver E. Jager, *Min. and Scientific Press*, June, 1919, p. 875.

† Austin, *Min. and Sc. Press*, Feb. 1916.

The general practice in modern copper smelting may be briefly outlined as follows :—

1. Smelting the lump ore in blast furnaces.
    - (a) With previous roasting of part of the charge only.
    - (b) Without previous roasting by partial pyritic smelting.
    - (c) Without previous roasting by pyritic smelting.

Fines agglomerated by pot or blast roasting and briquetted roasted concentrate may also be charged with lump ore, as in (a).

2. Fines, flotation concentrates, etc., are roasted in MacDougall or other furnaces with mechanical rabbles, and the product is smelted in reverberatory furnaces.

3. Bessemerizing the matte from both blast and reverberatory furnaces, producing blister copper.

4. Remelting the blister copper in a reverberatory furnace, partially refining it, and casting it in the form of anodes.

At some works the copper is charged into the furnace whilst molten.

5. Treating the anodes in an electrolytic plant producing pure electrolytic copper and obtaining any gold or silver which the copper may contain.

6. Melting the cathodes in a refining furnace and casting the metal into wire-bar ingots, etc.

Examples of works in which these operations are carried out are given later.

The Blast Furnace.—This may be either round, oval, or rectangular in section. The rectangular type is absolutely necessary if a large output is required, as the diameter of a circular furnace is limited by the distance to which the blast can penetrate, which for ordinary blowers does not exceed 56 inches, and is usually not more than 42 or 48 inches. There are, however, some conditions and localities where circular furnaces may be employed with advantage, but they are not in general use, and even when comparatively small charges have to be worked the rectangular form is preferred.

All blast furnaces for copper smelting are water-jacketed.

The output of the furnace, whether round, oval, or rectangular, is dependent on the following factors :—

1. Area of furnace at the tuyeres.
2. Composition and physical condition of the ore.
3. Fusibility of the charge.
4. Volume of the blast.
5. Pressure of the blast.

Circular Blast Furnaces.—For the reason stated above circular furnaces are in but limited use. They are, however, employed in smelting oxidized ores for the production of “ black copper,” also for concentrating mattes, and in small works for ordinary ores.

They usually range in diameter from 36 to 48 inches in America and England, but at Mansfeld furnaces as large as 6 feet 2 inches in diameter are in use for smelting the roasted *kupferschiefer* for the production of rich matte and black copper.

Smelting Oxidized Ores.—Oxidized ores occur in but few localities in sufficient quantities to be smelted alone, and, as already pointed out, the slags obtained when they are thus smelted carry considerable amounts of copper which are lost; further, the consumption of coke is high, hence the operation is not advisable, except when the prevailing conditions are unfavourable for smelting for matte. On the other hand, these ores are extremely valuable for smelting with sulphide ores, as they assist greatly in increasing the grade of matte.

A typical furnace for smelting oxidized ore is shown in sectional elevation in Fig. 33. The water-jacket is of mild steel, and is cooled by water admitted a little above the bottom and passing out at the top. The curb is a sheet-steel casing sometimes made by prolonging the outer plate of the jacket below the water space. It rests on a cast-iron base plate supported on columns. The jacket is surrounded by a removable wind box to which the blast pipe is connected. There is a large circular opening in the base plate, closed by two drop doors.

The curb is lined with fire-brick, the drop bottom is also lined with the same material.

Within the brickwork there is a lining of brasque (a mixture of fire-clay and ground coke or charcoal). There are six tuyeres, and opposite each in the wind box is a peep hole covered with a movable mica plate for observing their condition. The taphole at the bottom of the crucible is for the removal of the black copper, and that near the top for the outflow of the slag. The blast usually has a pressure of 12 to 14 ozs., and is supplied from a blower of the Root type.

The operations of charging and working the furnace are conducted in a similar manner to those for matte smelting, but the copper and slag are withdrawn as soon as sufficient of either has accumulated, the former being run into iron moulds and the latter into a slag pot. The black copper will contain from 95 to 98 per cent. of copper, and the slag not less than 1·5 to 2·5 per cent.

In smelting for black copper in Japan, the author has always added a small quantity of pyrites to the charge to prevent the formation of copper silicate, a little matte will be produced, but the slags will be poorer in copper than without this addition.

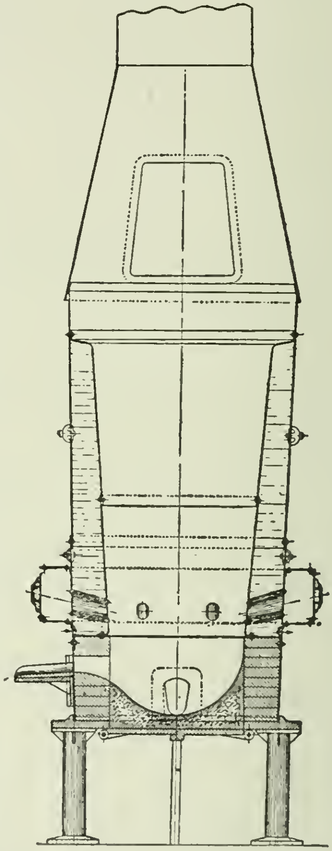

Fig. 33.—Round Water-jacketed Copper Blast Furnace (Fraser & Chalmers).

The largest furnaces hitherto used for smelting oxidized ores for black copper are in use at the mine of the Union Minière du Haut Katanga, at Lubumbashi, Belgian Congo. The Katanga furnace has two tiers of jackets, the lower ones being of the knee type, 10 feet high and 24 inches wide. It is 44 inches wide and 240 inches long at the tuyere line. The bosh begins about a foot above the centre of the tuyeres, and continues to the top of the lower jackets, where the furnace is 6 feet wide. The upper jackets are 7 feet 4 inches high. There are 20 tuyeres 4 inches in diameter on each side. The blast is heated by the Giroux system of U pipes, placed at the top of the furnace above the charging floor, and around which the hot furnace gases pass.*

Rectangular Blast Furnaces.—The dimensions of rectangular furnaces are very variable, the tuyere area generally ranging from 36 by 72 inches to 56 by 180 inches and 48 by 210 inches, and the amount of material smelted from 80 to 600 tons or rather more in twenty-four hours. In the following table are given some particulars of typical modern furnaces. In considering these it must be borne in mind that the charges are not of similar materials, so that the figures are not strictly comparative, yet they undoubtedly show the advantage of employing furnaces of large size.

Very wide furnaces, say 56 inches at the tuyere zone, are not advisable, except when the ore is coarser, having had the finer removed by screening, and a considerable depth of burden is carried above the tuyeres.

MODERN BLAST FURNACES.

	Dimensions at Tuyeres.	Number and Size of Tuyeres.	Centre of Tuyere to Feed Floor.	Height of Smelting Column.	Pressure of Blast.	Approximate Capacity.
					Ozs.	Tons per day
Anaconda, Washoe, .	56″×1044″	150, 4″ dia.	19′	..	40	3,000
Cananea, Mexico, .	48″× 210″	36, 4¾″ ,,	10′ 4½″	9′	16	280
Garfield, Utah, .	48″× 240″	..	..	10′	24	360
Mammoth, Cal., .	50″× 180″	34, 4¾″ ,,	..	9′	42	400
Steptoe, Nevada, .	42″× 240″	48, 4″ ,,	..	..	40	300 to 500
Cerro de Pasco, Peru,	56″× 180″	28, 4″ ,,	..	..	24	300
Mason Valley, Nevada, .	47″× 300″	50, 4″ ,,	..	12′	42	720
Teziutlan, Mexico, .	54″× 240″	40, 5″ ,,	14′ 6″	..	28 to 32	500

A general view of a small modern furnace having a capacity of about 200 tons in twenty-four hours is shown in Fig. 34.

Its chief dimensions are as follows:—Area at tuyeres 44 inches by 140 inches, height of charging floor above centre of tuyeres 12 feet.

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* *Eng. and Min. Journ.*, Oct. 1916.

The foundation is best on rock, but this is not always available, and generally an excavation to a depth of several feet is required, in which a bed of concrete should be put down with several courses of brickwork above it, and this should extend to at least 3 feet beyond the columns supporting the upper part of the furnace.

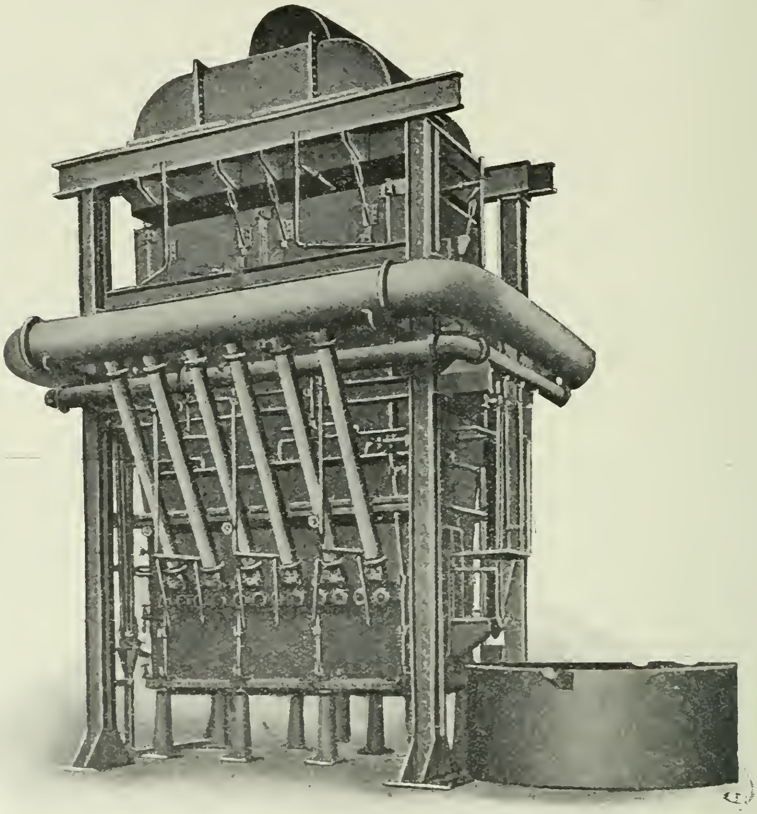

Fig 34.—Rectangular Water-jacket Copper Furnace.*

There are 24 tuyeres, 12 on each side, each tuyere pipe serving two tuyeres. The details of the construction of blast furnaces vary at different works, but generally they are as follows :—

The sole plate is supported on columns, and on this plate the bottom

* Fraser & Chalmers' Catalogue

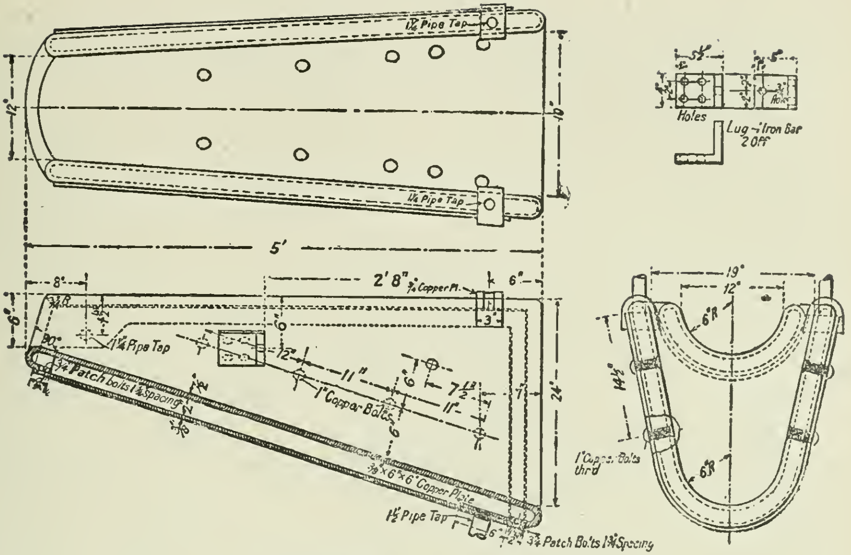
1¼ Pipe Tap
12"
16"
1¼ Pipe Tap
5'
8"
2' 8"
⅞ Copper Pl.
6"
6"
3"
30°
1¼ Pipe Tap
12"
11"
1" Copper Bolts
7½
11"
24"
¾ Patch bolts 1¾ Spacing
⅜×6×6 Copper Plate
1½ Pipe Tap
¾ Patch Bolts 1¾ Spacing
5½"
5"
Holes
Lug-1" Iron Bar 2 Off
19"
12"
6"R
14½"
6"R
1" Copper Bolts thr'd

Fig. 35.—Slag Spout, Cananea.*

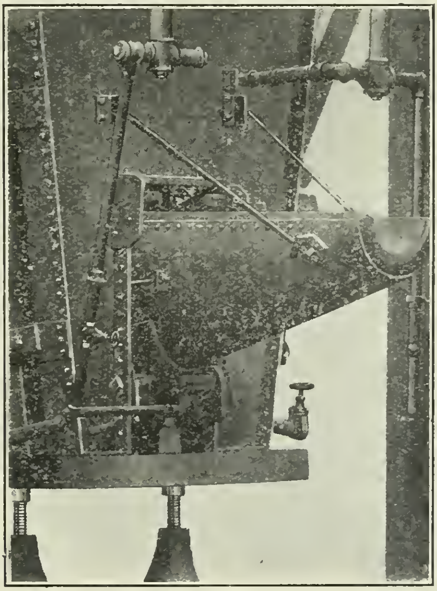

Fig. 36.—Slag Spout, showing method of support, etc.†

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* *Eng. and Min. Journ.*, April, 1908.

† Levy, *Modern Copper Smelting*, p. 161.

is formed of 9-inch bricks closely set together. In some furnaces the sole plate is supported by screwjacks, which are sometimes carried by a bogie to facilitate removal of the bottom when necessary.

The water-jackets, which are of mild steel, are usually in two tiers except at one end and sometimes also in the middle of the front where there is an extra jacket, both of small size, and each carrying a trapped spout. These latter jackets are placed in these respective positions, so that they can be easily taken down when required, and when accretions which have formed in the hearth require removal, etc. At the top of the jackets is often a course of two layers of fire-brick, and above this the cast-iron apron plates by which the charge is made to slide in the direction of the centre of the furnace, so that the fines may keep as much as possible in the middle line.

The jackets are supported by I beams fitted to the main upright columns, the sole plate can hence be removed leaving the jackets in position. The upper part of the furnace or stack is carried on a mantel plate of I beams supported by the upright columns. This is surmounted by a hood of brickwork, or sometimes of plate iron, from which the iron downtake leads to the flue and the dust chambers. There are two doors on each side of the stack at the charging floor level for charging, barring down accretions, etc.

The air is brought from the blowers in a blast main, the size of which depends on the number of furnaces in the plant, and thence by branches to the bustle pipe of each furnace. In the furnace illustrated the bustle pipe is 20 inches in diameter, and connects with the tuyeres by sheet-iron pipes as shown.

The pressure of the blast is from 16 to 24 inches. The trapped spout or discharge spout, through which the slag and matte flow continuously during the working of the furnace, is shown in Figs. 35 and 36. These spouts are made of cast iron, steel, sometimes of copper or bronze. During working they are always full of slag and matte, and thus the blast is trapped and prevented from escaping through the taphole. They are cooled by a supply of water through pipes independent of the jackets.

The hearths of furnaces for smelting sulphide ores are not lined with fire-brick and brasque as in the furnace for smelting oxidized ores, as such a lining would be rapidly cut away by mattes poorer than 35 per cent. of copper. The sides of the hearth are formed by the water-jackets, and only the bottom is made by a 9-inch layer of fire-brick set on end.

The radiation of heat from this bottom when the furnace is working causes a layer of matte to solidify upon it, and this forms the actual working bottom of the hearth.

In some furnaces only a thin layer of fire-bricks is laid on the bottom plate, and it is then water cooled.

Intermittent tapping should always be avoided and no large accumulation of molten material should be allowed inside the furnace, but the matte and slag should flow out continuously and be separated outside the furnace in a forehearth or settler.

As examples of large blast furnaces, the eight at Cananea are excellent types. One of them is shown in side and end elevation in Figs. 37 and 38.* Its dimensions are as follows :—48 inches by 210 inches at the tuyeres and

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* *Min. and Scientific Press*, April, 1908.

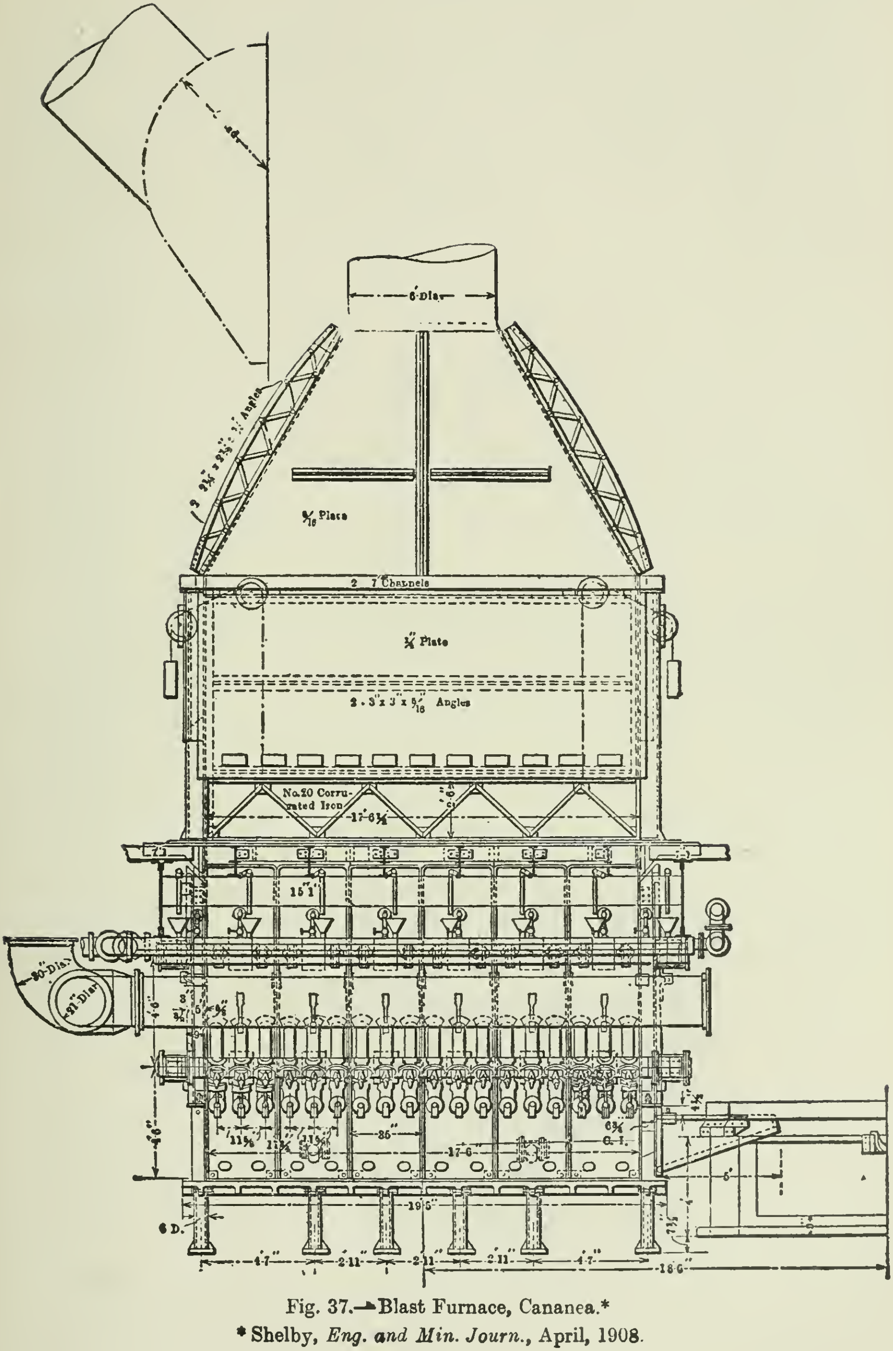

6' Dia.
9/16" Plate
2 7" Channels
3/4" Plate
2 - 3" x 3" x 5/16" Angles
No. 20 Corrugated Iron
17'-6 1/4"
15' 1"
30" Dia.
27" Dia.
4'-6"
11 5/8
35"
17'-6"
6 3/4
C. I.
19'-5"
6 D.
4'-7"
2'-11"
18'-6"

Fig. 37.—Blast Furnace, Cananea.*

* Shelby, *Eng. and Min. Journ.*, April, 1908.

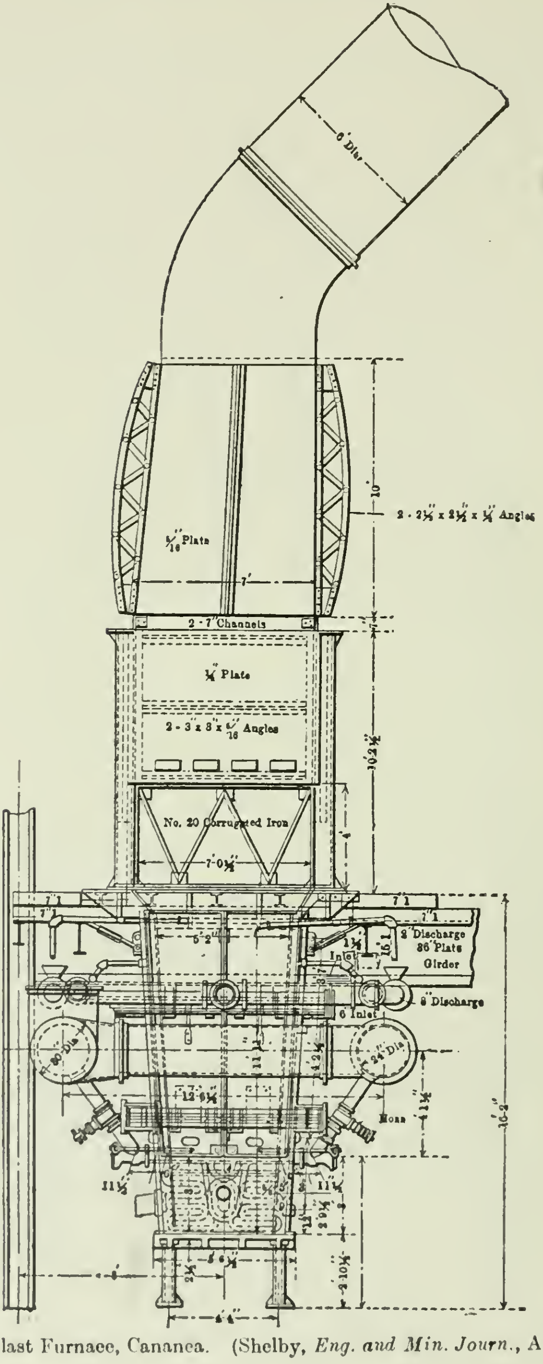

6' Dia.
10'
2 - 2½" x 2½" x ¼" Angles
5/16" Plate
7'
2 - 7" Channels
¼" Plate
2 - 3" x 3" x 5/16" Angles
10' 2½"
No. 20 Corrugated Iron
4'
7' 0½"
7" I
7" I
7" I
7" I
6' 2"
2" Discharge
36" Plate
Girder
Inlet
8" Discharge
6" Inlet
30" Dia.
24" Dia.
12' 0½"
Hose
11½"
16' 2"
11½"
11½"
2' 9½"
2' 10½"
5' 6½"
2½"
4' 4"

Fig. 38.—Blast Furnace, Cananea. (Shelby, *Eng. and Min. Journ.*, April, 1908.)

5 feet 2 inches by 7 feet at the upper end of the jackets. Height from the base plate to the charging floor, 13 feet 6 inches.

There are six water-jackets on each side, each 12 feet 6 inches high, and two water-jackets on each end 9 feet 7 inches high. The object in making these long jackets, instead of shorter jackets in two tiers, is to avoid the accumulation of scale or sediment on the bottom of a jacket where directly exposed to fire. The breast jacket at the end of the furnace is a solid cast-iron block, containing a heavy wrought-iron pipe in coils for the circulation of the cooling water.

The lower part of the furnace hood is not built of brickwork as usual, but is constructed of $\frac{1}{4}$-inch iron plates spaced 9 inches apart, forming an air-jacket open top and bottom around this part of the furnace.

There are 36 tuyeres, each being 5 inches in diameter. The height of the smelting column is 10 feet 3 inches measured from the centre of the tuyeres. The water enters the jackets at a temperature of 70° F. and leaves at 105° F.

The capacity of each furnace is 280 tons of wet gross charge per day, of which coke constitutes from 9 to 11 per cent. The charge, which is mixed at the ore beds, is delivered by a conveyor belt to a 75-ton storage bin which is provided for each furnace. This bin has five shoots which deliver into five 1-ton hoppers, each with a shoot so designed that the charge can be fed into the furnace, or may be dropped on the feeding floor for hand charging when necessary.

Blast pressure averages 16 ozs.

The gases from the furnaces pass to a main dust chamber 181 feet long, 60 feet broad, and 32 feet 6 inches high. From thence they pass by a flue 242 feet long, 20 feet wide, and 19 feet 6 inches high, to another dust chamber 84 feet long, 34 feet wide, and 23 feet 6 inches high, and then to the chimney stack. The stack is of steel, 19 feet 9 inches in diameter, lined with 9-inch bricks, and 190 feet high.

The charge contains Fe 26·5 per cent., Cu 6·39 per cent., and S 17·11 per cent.

The matte produced averages about 37 per cent. copper.

Further details regarding the construction of the blast furnace, its accessories, and its work will now be considered.

Water-jackets.—The water-jacketing of copper-smelting blast furnaces was adopted to avoid the frequent repairs required in the old fire-brick furnaces due to the burning out of their sides, especially just above the tuyere area, and is now universal.

The chief advantages which have followed the introduction of water-jackets are :—

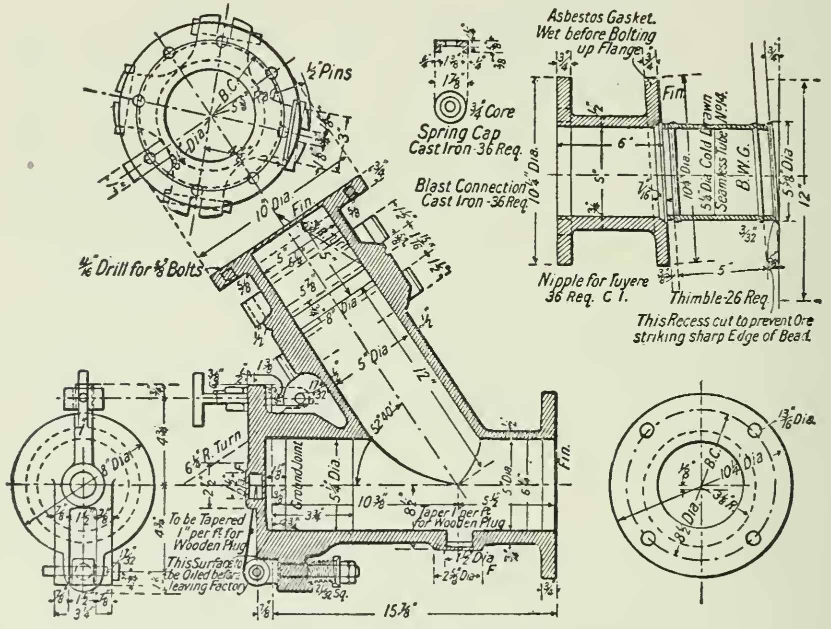
1. Repairs to the furnace are very greatly diminished.
2. The furnace preserves its shape and hence works with greater uniformity.
3. Accretions are more easily removed than in brick furnaces.
4. Larger furnaces can be built.
5. Rapid driving, and hence increased output is possible.

Water-jackets are best constructed of mild steel plate, the inner sides being usually $\frac{5}{16}$ to $\frac{3}{8}$ inch in thickness, and the outsides $\frac{1}{4}$ to $\frac{5}{16}$ inch. The water space ranges from 4 to 5 inches. The inner side is sometimes made of thick sheet copper to prevent corrosion by sulphates. The plates should be flanged outwards so that rivets, welds, etc., should be outside the furnace.

Cast iron should never be used as a material for jackets, owing to its liability to crack. Formerly the jackets were in three tiers, but in many modern furnaces they are in two tiers only, those of the lower tier being from 7 to 10 feet high, and of the upper tier from 4 feet 6 inches to 7 feet 6 inches.

The end jackets are perpendicular, while the lower tier of the side jackets is boshed.

The water for cooling the jackets should, whenever possible, be so arranged that each has its own supply, at some works, however, as at Granby, the lower jackets are fed from the discharge from the upper.


½" Pins
B.C.
Dia
10" Dia.
Fin
11/16" Drill for ⅝" Bolts
¾" Core
Spring Cap
Cast Iron - 36 Req.
Blast Connection
Cast Iron - 36 Req.
Asbestos Gasket.
Wet before Bolting up Flange
Fin
10¼" Dia.
6"
5"
5¼" Dia. Cold Drawn Seamless Tube No. 14 B.W.G.
5⅜" Dia
12"
5"
Nipple for Tuyere
36 Req. C I.
Thimble - 26 Req.
This Recess cut to prevent Ore striking sharp Edge of Bead.
8" Dia
5" Dia
12"
52°40'
6½" R. Turn
8" Dia
To be Tapered 1" per ft. for Wooden Plug
This Surface to be Oiled before leaving Factory
Ground Joint
5¼" Dia
10⅜"
Taper 1" per ft. for Wooden Plug
1½" Dia
2⅜" Dia
F
Fin.
15⅞"
3¼
13/16" Dia.
B.C.
10½" Dia
3½" R.
8½" Dia

Tuyere - 36 Req. C I

Fig. 39.—Tuyere, Cananea Blast Furnace.*

The water should not be fed into the jackets near the bottom, but at some distance above. In the furnace at Cananea, an extreme case, the inlets of the 12-foot 6-inch jackets are only 23 inches from the top. The outlets for the discharge of the hot water should, of course, be at the top.

The temperature of the discharge water should be about 85 to 105° F. to avoid too great an abstraction of heat from the furnace.

The tuyere openings in the jackets are lined with mild steel carefully fitted by flanging on the inside and riveting on the outside.

The Tuyeres.—These are of various forms, and range from 3 to 6 inches in diameter, according to the size of the furnace. They are usually spaced about 12 inches apart in the side jackets, there being none in the ends.

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* *Ibid.*

A typical tuyere in use at Cananea is shown in Fig. 39.

The Blast.—For the supply of air to copper blast furnaces blowers of the Root or Sturtevant type are in practically universal use; turbo blowers have, however, been introduced at Mount Lyell and Rio Tinto, and are said to give satisfactory results.

As to the amount of pressure of the air required no definite rule can be laid down, as so much depends on the size of the furnace and the conditions under which it is working.

A definite amount of fuel is necessary for smelting each ton of the charge and for the combustion of this fuel a definite volume of air is needed per minute, and so long as this volume of air is blown into the furnace the pressure is immaterial and will vary according to the frictional resistance of the charge.

A copper blast furnace ordinarily requires 200 to 350 cubic feet of air per minute per square foot of area of the tuyere zone. For each given furnace there is a maximum volume of air, and when this has been determined it should be adhered to.

In modern large furnaces a pressure of blast of from 40 to 50 ozs. is not uncommon, whilst in those of medium size 16 to 24 ozs. is usual.

Fuel.—The fuel in almost universal use in blast furnaces smelting copper ores is coke; anthracite is, however, sometimes used, as in the 30-foot furnace blown in by the Northern Peru Mining Co. in 1927. The amount of coke ordinarily used ranges from 13 to 17 per cent. of the charge; a " common ratio is 6 charge : 1 coke." *

In pyritic smelting, however, only a small amount, from 1 to 3 per cent., is usually required. On the other hand, pyritic smelting furnaces have been worked from time to time without the addition of any coke.

The use of pulverized coal to replace a large proportion of the coke in blast-furnace smelting has been the subject of extensive experiments at the Tennessee Copper Company's Smelter at Copperhill, Tenn., and the International Nickel Company's Smelter at Copper Cliff, Ontario. An excellent account of these experiments is given by E. P. Mathewson and W. L. Wotherspon in the *Bulletin of the Canadian Mining Institute* of July, 1919, to which reference should be made for details.

The pulverized coal is injected into the furnace through the tuyeres by the air blast.

The authors say, " To summarize the results of the experiments at Copper Cliff and Copperhill, it can be said that under difficult conditions it has been demonstrated that important economies are possible at many smelting plants by the utilization of pulverized coal, thus replacing a considerable portion of the coke."

One of the principal difficulties in using powdered coal has been to design a proper tuyere which will provide for the injection of coal as well as air supply. One of the latest methods adopted to overcome this difficulty is to inject coal through openings between and slightly above the level of the tuyeres, thus introducing a mixture of coal and air into the furnace independent of the main air supply.

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* Hofman, *Metallurgy of Copper*, p. 182.

The Forehearth or Settler.—In smelting sulphide ores for matte it is of great importance, in fact absolutely necessary, to allow the matte and slag to flow out of the furnace continuously as they are formed, as their separation within the furnace is imperfect, and in intermittent tapping the hearth is liable to be filled up with accumulations of half-fused products difficult or impossible to remove without stopping the furnace. External settling is hence now practised at all modern works. The special functions of the settler are not only to give opportunities as regards time, rest, and space for the quiet settlement of the matte, but also to act as a reservoir for it for the converters in works where Bessemerizing is practised, and thus save the cost of remelting. For furnaces of small size the separation is sometimes effected in one or more large cast-iron pots or portable settlers. When the former are in use the slag and matte flow into a very large pot from which the slag overflows into a smaller pot on wheels by which it is taken to the dump, the matte being tapped out from the larger pot and cast into slabs when sufficient has accumulated.

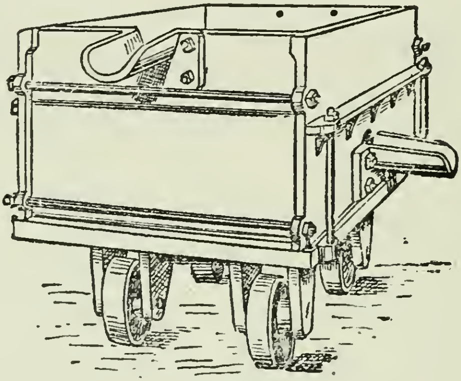

Fig. 40.—Portable Settler.

For furnaces of moderate size a portable settler or forehearth, such as that shown in Fig. 40, is frequently employed.

It is a rectangular box, sometimes circular, of cast or wrought iron or mild steel, lined with 4½- or 9-inch fire-brick and with a cover similarly lined. Dimensions about 5 feet by 5 feet 6 inches. A little above the bottom is the taphole for matte and at the top just below the cover the spout for the overflow of the slag. The matte is tapped from time to time, and the slag overflows more or less continuously into a slag pot for transport to the dump as just described.

The settlers required for most modern furnaces are, however, too large to be portable, and are hence fixed.

A typical example, one of those in use at Cananea, is shown in Fig. 41.*

It is placed between two of the blast furnaces, each of which is 210 inches by 48 inches at the tuyeres, and receives the slag and matte from both. It consists of a mild steel oval shell without bottom, with parallel sides 8 feet 6 inches in length and ends of 7 feet radius. The total length is thus 20 feet 6 inches. The breadth is 14 feet 6 inches and the height about 5 feet.

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* Shelby, *Eng. and Min. Journ.*, April, 1908.

The bottom is made of 10-inch refractory brick, the upper layer below the spouts and tapholes being replaced by chrome brick. The sides have a packing of 12 inches of crushed quartz and clay next the shell, then 9 inches of chrome brick.

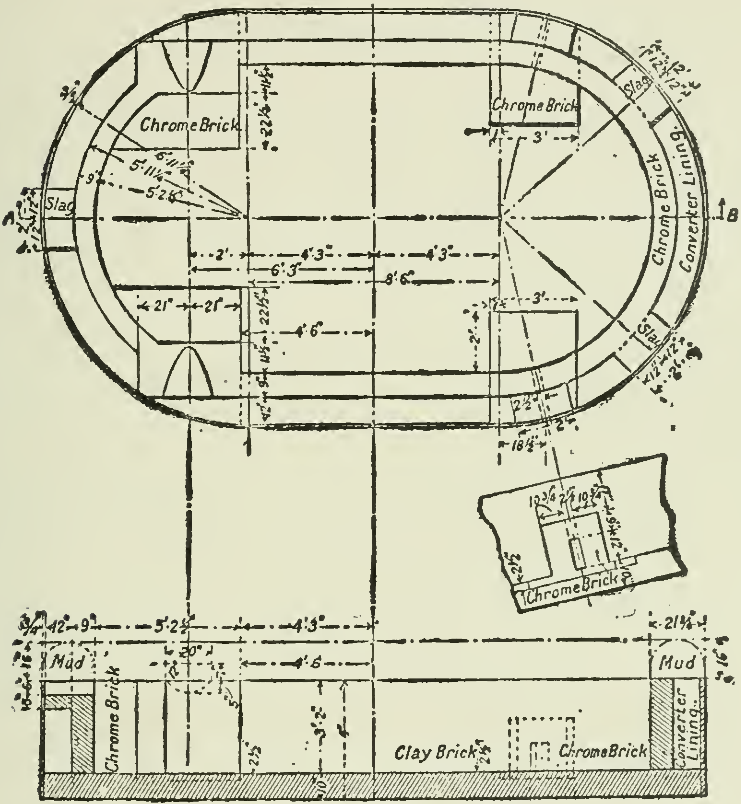
Chrome Brick
Chrome Brick
Slag
Slag
Slag
Chrome Brick
Converter Lining
A
B
5'11½"
6'11½"
5'2½"
9"
22½"
2'
4'3"
4'3"
6'3"
8'6"
21"
21"
22½"
4'6"
3'
3'
2'
18½"
2½"
Chrome Brick
12"
9"
5'2½"
4'3"
20"
4'6"
21½"
Mud
Mud
Chrome Brick
3'2"
Clay Brick
Chrome Brick
Converter Lining
10"

Fig. 41.—Settler, Cananea.

This forehearth has two spouts by which the slag overflows and two water-jacketed bronze tapholes at the opposite end, through which the matte is tapped as required for the converters. The settlers at the Washoe plant are 16 feet in diameter and 5 feet high. They are constructed of $\frac{1}{2}$-inch steel plates lined with 18 inches of silica brick with a filling of 4 inches of ground quartz between the shell and the brick lining. The bottom is covered with 12 inches by 6 inches by 3 inches silica bricks overlaid with a layer of ground quartz. A water pipe perforated with holes encircles the settler outside near the top for the purpose of cooling the sides when necessary.

These large settlers are usually without a fixed cover, the chilling of the slag and matte due to radiation being prevented by the coating of solidified slag which covers the surface and upon which at some works a layer of coke dust is spread. The matte is tapped periodically in quantities of 5 or 10 tons usually into a ladle by which it is carried by an overhead electric travelling crane, or on rails to the converters. But in some works it is tapped directly into them, loss of heat being thus prevented. The slag in some cases, as it flows from the settler, is granulated.

At Mt. Lyell the stream of slag is struck by a jet of water from a 1-inch pipe with a pressure of 60 lbs. per square inch, the granules dropping into a launder.

Large settlers of the same form and construction as those used at blast furnaces have been installed at the reverberatory furnaces at Great Falls, Montana, and other works, and the losses of copper in the slags are less than when the furnaces were simply skimmed.

At some works the settler is a reverberatory furnace heated by its own fire-place. The separation of slag and matte is then very complete; the matte is always ready for the converter in any quantity that may be desired, and can be stored without danger of chilling when the converters are running irregularly, or are temporarily stopped.

Dust Chambers.—The losses which may arise from the escape of fine particles of ore which are carried out of the furnace with the gases are often very considerable, hence all well-arranged plants should be provided with capacious flues and large dust chambers for their settlement and collection.

These losses are especially large when a high pressure of blast is used, when the charge contains much fine material, and when the stock line or top of the smelting column is much below the charging doors. At but few works they are less than 5 per cent., whilst at others they are as much as 10, and in exceptional cases reach 15 or 20 per cent. or even more. The dust is, too, often richer in copper than the coarse ore of the charge.

The conditions necessary for the deposition and collection of this dust are the same as those described under "Lead" (p. 221), and need not be recapitulated. The chief factor may, however, be mentioned—viz., slow movement of the furnace gases. To that end, the flues must be of large dimensions and the dust chambers very capacious. As regards the latter a large area of the cross-section of the chamber is more important than length.

In experiments made at the Copper Queen, it was found that with velocities of 150 feet per minute and less, the very fine dust would settle in comparatively short distances, and with wire screens at 3 feet intervals equally good settling was obtained at twice the velocity.

When the gases contain lead or zinc fume a bag-house plant is necessary for their collection, but is only in use at one or two copper works. An example of a system of flue-dust collection is afforded by the Cananea smelter described on p. 103.

Dust may also be separated and collected from the flue-gases by the Cottrell process of electrostatic precipitation.

The principle of the electrostatic fume-settler devised by Cottrell may be stated as follows :—

If needle points connected with one side of a high potential direct-current line are opposite a flat plate connected to the opposite line, the intervening space becomes highly charged with electricity of the same sign as the points, and any insulated body brought into this space instantly receives a charge of the same sign as the points. If these bodies are free to move, as is the case with dust and fume, they will be repelled from the points and be attracted to the plate, and will move at a rate proportional to the charge and the potential gradient between the points and the plate. Installations are worked at 50,000 to 75,000 volts.

The construction and arrangement of the electrodes, as also of the chamber containing them, naturally vary widely with the conditions to be fulfilled. All plants thus far erected may, however, for convenience be classified under two general heads—those in which the collecting electrodes are plates hung in a flue with discharge electrodes between them, and those in which a system of pipes carrying the gases act, as the collecting electrodes themselves, one or more discharge electrodes being placed axially within each. There has been a distinct tendency toward the latter type in new installations, largely on account of facility of construction.

At the Ashio Copper Smelter in Japan, two Cottrell treaters were installed in 1918 ; one, the main treater for dealing with the gases from four M'Dougall roasters, two blast furnaces, and four converters, and the other, for treating the gases from a large reverberatory furnace with waste heat boilers. The main treater consists of ten sections, each containing 64 riveted pipes, arranged in a square, making a total of 640 pipes. The pipes are 16 feet long, 12 inches inside diameter, and are made of No. 16 sheet-steel. The volume of gas handled by it is somewhat in excess of 150,000 cubic feet per minute. The amount of dust collected varies from 6 to 10 tons per 24 hours.*

The dust from the flues and dust chambers termed " flue dust " is not a desirable material for smelting, yet it has to be dealt with. It may be smelted in certain proportions with the reverberatory furnace charges, or may be mixed with the charges for sintering or briquetting, but generally gives rise to difficulties in any of these operations. Two examples of its treatment to render it suitable for blast-furnace smelting are as follows :—

At the Tennessee Copper Company's works the poor matte, which is resmelted pyritically, is poured on a bed of flue dust, and over each pot of poured matte is spread a car of flue dust. Another pot of matte is poured on this and another car of flue dust spread on it, and this is repeated until the mixture is about a foot in thickness.

At the Copper Queen the flue dust is incorporated with molten converter slag in a revolving drum of the shape of a truncated cone, both being delivered together into the small end of the machine (Lee).

The amount of flue dust is greatly diminished by smelting the fine ore and concentrate in reverberatory furnaces, coarse or lump ore, or briquetted fines, only being charged into the blast furnace.

Working of the Blast Furnace.—In the ordinary smelting of sulphide ores the charge may consist of roasted ore mixed with varying proportions of raw ore ; or of raw ore with oxidized ores, when the latter are available :

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* Ritaro Hirota and Kyoshi Shiga, *Min. and Scientific Press*, Feb. 14, 1920.

and in all cases with the addition of siliceous gold and silver ores when these can be obtained. The greater number of copper smelting plants, however, now utilize part of the sulphur of the pyrites as fuel and smelt these ores without previous roasting. Part of the coke is thus replaced by the sulphur of the pyrites, and the blast is suitably arranged to burn both. This is termed "partial pyritic smelting," to distinguish it from "pyritic smelting," in which but a very small quantity of coke is used and the chief fuel of the furnace is the sulphur of the pyrites.

In small blast furnaces the charging is done by hand, but in large furnaces generally by means of cars which are usually side tipping. At many smelters, even those with very large furnaces, the coke is fed in from barrows.

At the smelting works of the Teziutlan Copper Company (Mexico), above each furnace is a 65-ton bin or charging hopper into which the contents of the charge cars are dumped.

The bins above the furnaces are divided by five vertical plates into sections. These dividing plates extend about half-way up the bin. Each of the sections has two gates, each gate operated separately by means of a hydraulic cylinder controlled from a bank of levers in front of the furnace.

By looking into the furnace it can be seen at what point additional charge is required, and the corresponding gate opened to admit more material. The furnace may thus be fed at 10 different points independent of all others.

At Cananea also each furnace is charged from a bin (see p. 103).

The weight of the charge varies with the size of the furnace, and ranges from 5 or 6 cwts. to 2 tons or more.

The flux is charged in together with the ore.

The coke, of which usually from 7 to 12 per cent. is required, is then fed in, care being taken to distribute it where it is most required, and it is important that as little as possible should be used.

It is also of the first importance that the lump and fine ore should be properly distributed. The charging should hence be effected in such a manner that the "fines" go to the centre and the coarse to the sides of the furnace. The charge is thus kept open at the sides and the tendency to scaffolding diminished

The depth of the smelting column depends in great measure on the percentage of iron in the ore and the character of the fuel, highly ferruginous ores having a shorter column than those which are less ferruginous to avoid reduction of the iron. It is usually from 8 to 10 to 14 feet from the tuyeres to the top of the charge or the stock line, and this varies from 1 to 3 feet below the charging doors.

The charges are arranged whenever possible so that a matte containing about 30 to 40 per cent. of copper and a slag containing about 40 per cent. of silica will be produced. Since the introduction of Bessemerizing in basic converters, such a high-grade matte is not necessary (see p. 127). As regards the slag any percentage of silica between 25 to 55 per cent. is admissible under favourable conditions as to the bases present.

When the charges are properly constituted and properly fed in, the furnace will work smoothly and require but little attention except punching of the tuyeres, and sometimes, if much fine concentrate is being worked, barring down accretions with heavy iron bars. The matte and slag run out continuously into the settlers. The latter should contain less than 0·5 per cent. of copper.

The furnace gases are discharged through the downtake to the flues by which they are led to the dust chamber, and thence to the chimney stack. In some works they pass to a sulphuric acid plant, where the SO_2 which they contain is converted into that acid for sale (see p. 117).

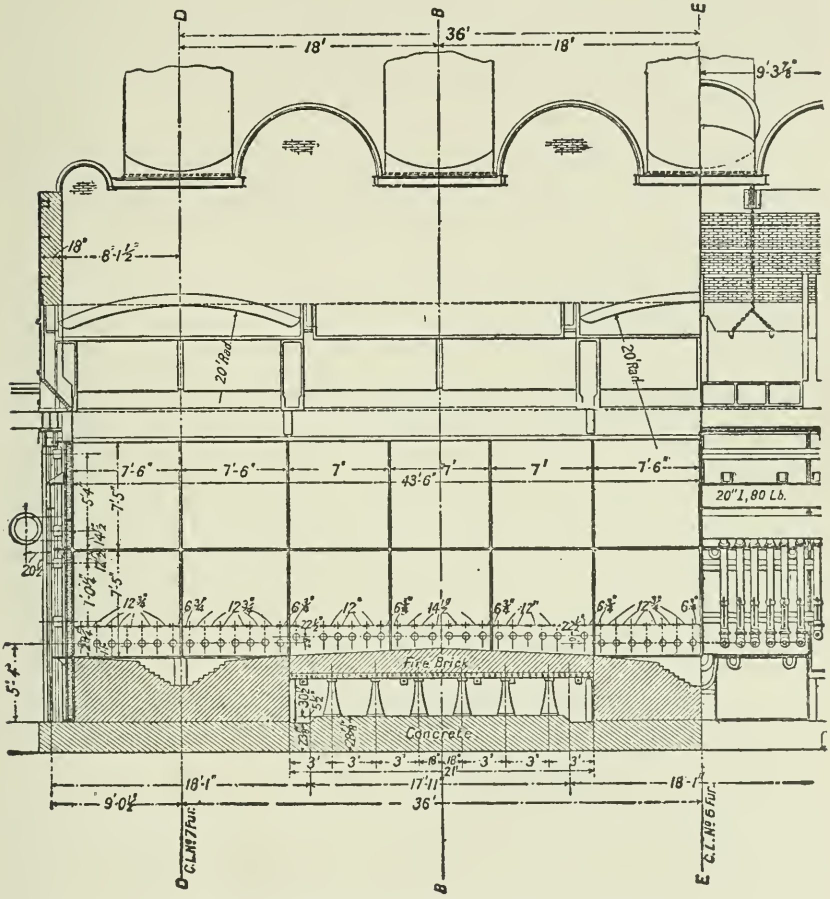
D
B
E
36'
18'
18'
9'-3⅞"
18"
8'-1½"
20' Rad.
20' Rad.
7'-6"
7'-6"
7'
43'-6"
7'
7'
7'-6"
20" I, 80 Lb.
Fire Brick
Concrete
5'-4"
3'
3'
3'
18"
18"
21"
3'
3'
3'
18'-1"
17'-11"
18'-1"
9'-0½"
36'
C.L.No. 7 Fur.
C.L.No. 6 Fur.

Fig. 42.—Eighty-seven-foot Blast Furnace, Anaconda.

The Blast Furnaces of the Washoe Plant of the Anaconda Company.— These furnaces are the largest in the world. The former plant consisted of seven furnaces, each 4 feet 8 inches by 15 feet area at the tuyeres. As increased capacity was required, Mr. Mathewson joined two of these furnaces into one by removing their opposite ends, enclosing the space between them (21 feet) within water-jackets, and providing a suitable bottom and superstructure. The two 15-foot furnaces thus became one furnace 51 feet in length, the width remaining the same. Two others were similarly joined. Owing to their success, the three remaining furnaces were united in the same way to form a furnace 87 feet in length. The tapholes and settlers of the old furnaces remain and are used for the discharge and separation of the matte and slag as before. Thus the 51-foot furnace has two tapholes and settlers, and the 87-foot furnace three of each. The spaces between the old furnaces are furnished with bottoms of fire-brick higher than the old bottoms, but sloping towards them.

The 87-foot furnace is shown in longitudinal section and part elevation in Fig. 42.*

The 51-foot furnaces smelt on an average about 1,600 tons in twenty-four hours, or about 6·72 tons per square foot of hearth area, whilst the 87-foot furnace smelts about 3,000 tons, which is equivalent to 7·5 tons.

The advantages shown in practice by these large furnaces are :—

(*a*) Saving of space.

(*b*) Saving of fuel and labour.

(*c*) Comparative freedom from accretions or "scaffolds." The long walls afford but little support for accretions, and when formed they are easily barred off.

(*d*) Higher temperature in the furnace, hence the matte and slag are hotter, and slags can be run higher in silica.

The furnaces are charged with ore, etc., from a train of special cars alternately on either side. The coke is tipped in from barrows. The matte and slag run continuously through the trapped spouts into the settlers through a hole in their slag roofs. The matte is tapped as required into a 9-ton steel ladle which runs on rails above the converters. The slag overflows through the slag hole at the top of the settler, and is granulated by a stream of water from a 6-inch pipe somewhat flattened at the end.

The matte runs on an average about 46 per cent. of copper, and the slag 0·2 to 0·3 per cent.

The blast for the three furnaces is supplied by 10 Connersville rotary pressure blowers which furnish about 60,000 cubic feet of air at a pressure of about 40 ozs. per ton of ore smelted.

Pyritic or "Raw Sulphide" Smelting.—The term pyritic smelting should be restricted to that form of matte smelting in which by far the greater portion of the heat required for fusion is derived from the oxidation of the iron sulphide contained in the ore. In no case has it been found practicable to obtain continuously the whole of the heat required from the constituents of the ore alone. A small amount of coke, 1 to 2 per cent. at least, is always necessary.

When the amount reaches or exceeds 5 or 6 per cent. the process becomes that of "partial pyritic" smelting.

The object of the process is to make a more or less high-grade matte from low-grade sulphide ores without previously roasting them. Its most important feature commercially is its low cost compared with ordinary smelting, as the operation of roasting is dispensed with, and only a very small quantity of coke is required.

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* Levy, *Modern Copper Smelting*, p. 128.

The ores suitable for the process are those containing sufficient iron pyrites or pyrrhotite to give the heat required, with enough copper pyrites to yield the necessary matte output, and containing sufficient free SiO_2 to flux the iron which is oxidized. The SiO_2 must be free, and not combined as in felspar, diorite, and the like.

If the ores are too rich in sulphides, then quartz, or preferably siliceous ores containing gold and silver, should be obtained to mix with them, or only a very low rate of concentration—*i.e.*, a poor matte—will result. On the other hand, if poor in sulphides, sulphide ores must be procured to add to the charge.

The process is of special importance for the treatment of pyritic ores carrying small quantities of gold and silver with sufficient copper to ensure a matte which will collect the precious metals.

The presence of, at least, about 0·5 per cent. of copper is necessary as a pure iron matte is only an imperfect collector, and the richer the ore is in gold and silver the higher will be the percentage of copper required. When the ores are of low grade, say about 2 per cent. of copper, it is rarely possible to obtain a matte of 40 per cent. suitable for Bessemerizing in an acid-lined converter; frequently it may contain only 10 or 20 per cent. of copper, which may be blown in a basic-lined converter. The matte is sometimes concentrated by pyritically smelting it, with the addition of silica or siliceous ores to flux the FeO formed, when a matte of 40 to 50 per cent. of copper will be produced.

This concentration is especially necessary where the matte has to be shipped for sale on account of the expenses of transport, the deductions made for subsequent treatment, and low price per unit of copper, as compared with richer matte. In concentrating a matte, limestone is sometimes used as a flux for the silica which is in excess of that required for the ferrous oxide, as it decreases the specific gravity of the slag, and thus promotes the clean separation of the matte.

Ores containing only 2 per cent. of copper or less do not usually pay to smelt unless they contain gold and silver or are first concentrated by dressing or flotation processes.

Galena and zinc blende in the ore are always undesirable. They tend to promote losses of silver by volatilization; the former, too, is liable to cause the ore to agglomerate, and the latter to produce infusible slags. Alumina in certain proportions is also objectionable, as it raises the melting point and viscosity of the slags, so that they flow sluggishly from the furnace. Metallurgists differ as to the limit to which these should be permissible, but the consensus of opinion is against more than 10 per cent. of zinc, 12 per cent. of lead, and as regards alumina great difficulties have been sometimes encountered with slag containing over 10 per cent.

As to whether cold or hot blast should be used the experience at Mt. Lyell and the Ducktown smelters indicates that hot blast is unnecessary for ordinary pyritic ores. If, however, the ore is so low in sulphur that 6 per cent. or over of coke is necessary for smelting them, then hot blast has been found to be beneficial at some smelters, but the process becomes "partial pyritic" smelting.

The Furnace.—The blast furnace for pyritic smelting may be of any good type for ordinary smelting with an external forehearth. An increase in the number of tuyeres is sometimes advisable, and generally they should be placed somewhat closer together than for ordinary smelting.

The Changes and Reactions which occur in the Process.—The essential substances in the ore are silica and iron sulphide (iron pyrites), together with a proper percentage of chalcopyrite. The iron pyrites FeS_2 gives up one atom of S by the action of heat alone in the upper part of the furnace becoming approximately Fe_6S_7, and as it descends it loses more S, becoming Fe_xFeS (iron sulphide and free iron), which is the true pyritic fuel of the furnace. According to Sticht none of the sulphur thus given off is oxidized until it reaches the free air above the charge when it burns, as the gases in the upper two-thirds of the furnace are neutral and not oxidizing, the oxygen of the blast being completely absorbed in the zone of fusion.

About 5½ to 6 feet above the tuyeres in the Mt. Lyell furnace, the sulphides melt.

Here it is that the Fe_6S_7 loses S and becomes Fe_xFeS, but there is still no oxidation. The molten iron sulphide is extremely liquid and runs down between the pieces of unchanged quartz or siliceous gangue to the oxidizing zone or *focus*. At this zone the tuyere region, and a little above it, the charge is supported by a network of pieces of quartz. Part of the molten iron sulphide, as it passes through the interstices between these pieces of quartz which are at a white heat, is instantly oxidized to FeO, and as instantly the FeO formed unites with the quartz forming an iron silicate slag, which with the remainder of the unoxidized sulphides falls into the crucible or hearth below the tuyeres. As it is at these interstitial openings that the O of the blast oxidizes the FeS there is a close analogy between the process and Bessemerizing.

The sulphur of the iron sulphide is oxidized to SO_2. The slag formed corresponds in composition to the silicate, the formation temperature of which corresponds with that prevailing in this zone. All the oxygen of the blast is expended in this oxidation of the iron sulphide, and none is left to effect any roasting of the pyrites in the upper part of the furnace.

According to Guess,* however, the oxygen in the air blown in is not all consumed in the zone of fusion, but some is always present in the upper part of the furnace and in the furnace gases.

The grade of matte depends on the amount of air blown into the furnace, but this amount must stand in proper relation to the proportion of SiO_2 present to flux the resulting FeO. So that if the amount of pyrites is increased in a charge without increase of the blast and of the SiO_2 this pyrites will go into the matte as FeS and lower its grade.

A certain number of pounds of oxygen will burn a certain number of pounds of FeS to FeO, always providing there is sufficient free SiO_2 to combine instantly with the FeO and form an iron silicate slag.

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* *Eng. and Min. Journ.*, November, 1912.

The amount of SiO_2 which the charge must contain depends on the amount of FeS which can be oxidized, and this depends on the amount of the blast. The volume of air blown in is thus of the first importance, and if, as is the case with some ores, 20,000 to 30,000 cubic feet of air per minute have to be forced in the pressure must be equal to the work even if it amounts to 50 ozs. or more, and, therefore, a piston blowing engine or Parsons' turbine blower, as in iron blast furnaces, is advisable, and not rotary blowers.

As the composition of the slag varies with the temperature at which it is produced and as the temperature is dependent on the amount of blast forced in per minute, therefore the pyritic furnace chooses its own slag, and its composition and the grade of matte adjust themselves automatically to the volume of air blown in and the amount of silica available for combining with the FeO formed.

In actual practice the SiO_2 in the slag ranges from 21 to 30 per cent. at Mt. Lyell and to 37 per cent. at the Tennessee Company's smelter. As regards the earthy bases, lime, etc., in the slags, 10 per cent. approaches the minimum. From what is stated above it is hence evident that the two essential points in the process are :—

There must not only be sufficient air blown in to burn the required amount of iron sulphide, but sufficient silica must also be present to combine at once with the resulting ferrous oxide.

A small quantity of coke is always added, at Mt. Lyell it is only 1 per cent., but this is an exceptionally low amount, and at the smelters at Ducktown, 2½ to 3½ per cent. is used.

The effect of this small amount of coke is partly to keep the charge open, but according to Sticht, heat is developed by the burning of the carbon by oxygen derived not from the oxygen of the blast, because no coke should reach the tuyere zone, but from the SO_2 in the zone above it, and this extra assistance appears to be necessary for the process.

Hence this small addition of coke does not lessen the oxidizing power of the furnace, but the heat developed assists in preparing the charge for the reaction in the oxidizing zone. If an excess of coke is added some will pass into the oxidizing zone and use up oxygen which should go to the FeS, a low grade matte will result, and the process becomes ordinary or at the least partial pyritic smelting. It is important to remember that true pyritic smelting has no heat to spare; the charge must hence be of such a composition that the slags are easily fusible.

As examples of pyritic smelting the practice at the following works may be cited :—

Mt. Lyell, Tasmania.[*]—At Mt. Lyell important modifications of the pyritic smelting process have been introduced, hot blast at moderate pressure has been abandoned, cold blast at high pressure adopted, and the smelting column has been raised to 18 feet above the tuyeres.

In this connection it may be mentioned that the new blast furnaces at Mt. Morgan, Queensland, have been erected so that a 25-feet column may be maintained if found desirable. The pressure of the blast is to be 4 lbs. per square inch.

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[*] *Eng. and Min. Journ.*, June, 1915.

The furnaces used at Mt. Lyell are 210 inches long and 54 inches wide. From 1,200 to 1,300 long tons are smelted per day in a little more than two furnaces. The ores consist of siliceous ore containing about 6 per cent. of copper and pyrites averaging about 0·5 per cent. The furnace charge averages from 2·15 to 2·25 per cent. of copper, and from this a 45 to 50 per cent. matte is obtained in one smelting. The copper content of the slag ranges from 0·35 to 0·45 per cent.

The materials to be smelted are brought to the furnaces by hand in charging carts, and are emptied out of the ends of the carts in a long string on the charging plate close to the edge of the furnace opening. The coke is brought first and pushed in, then the pyrites is dumped and shoved into the furnace, the siliceous ore is put in on top of it, then limestone, and finally slag, flue dust, and cleanings. Feeding is done at both sides of the furnace, and it is absolutely necessary to have the greatest elasticity in the delivery of the materials to it. The success in attaining the high concentration ratio and avoiding double smelting depends on this elasticity in the delivery of materials and proper feeding. It has been found that conveying appliances cannot do what the feeders have to do—use judgment in the selection and placing of the materials at the furnace. The only mechanical device used in feeding is an "iron man," which pushes the materials off the inner edge of the charging plate into the furnaces. This consists of a framework embracing each long side of the furnace. It slides and rolls on the charging plates in such a manner that a line of hinged pusher plates in front simply shoves the material over the furnace edge. The charges, or any ingredient thereof, may be placed wherever desired in the furnace by the wheelers dumping it at the spot indicated, thus blow-holes or unequal descent of the top may be promptly attended to. The practice at Mt. Lyell, modified by many conditions, is to feed so that the centre line of the furnace is porous, and the blast does not come up prominently on the jacket but rises out of the column evenly.

The charges are not calculated, as the calculation is of no special use for immediate running purposes, since the furnaces have to be manipulated according to the grade of matte which falls. This is tested at intervals by the furnace foremen, who have been taught to make a quick, rough determination of the copper by the cyanide method. The quantities of pyrites and of limestone are kept constant. The siliceous ore and coke are varied as required, but the variation is mainly in the amount of siliceous ore used. When the matte is below grade, more siliceous ore is put on. This is speaking generally. The coke used ranges from 3·5 to 5 per cent.; it contains 16 per cent. of ash. The tuyeres are not circular, but long and oval like a wide mouth, thus approximating to a continuous tuyere opening along the furnace sides. Each furnace receives 20,000 cubic feet of air per minute at a pressure of about 4 lbs. per square inch. The blast pressure has been increased by means of multi-stage turbo-blowers, so that a maximum pressure of 8 lbs. may be obtained if desired. The height of the smelting column as mentioned above is 18 feet, but it is considered that in the matter of height finality has not yet been reached.

The Tennessee Copper Company.—These works are situated at Copperhill, and consist of three blast furnaces 180 inches and four 270 inches long. Formerly all were 56 inches wide, but one of the former has been narrowed to 44 inches, and has been found specially suitable for the concentration of the matte from the first smelting.

The ore has approximately the following composition :—

Copper 2 to $2\frac{1}{2}$ per cent., iron 31 to 37 per cent., sulphur 20 to 30 per cent., silica 10 to 25 per cent., the remainder being lime 6 per cent., with small percentages of magnesia, zinc, and alumina. The height of the ore column is 10 to 12 feet. The smaller furnaces smelt 375 to 400 tons and the larger furnaces 500 to 600 tons of charge daily. The former are supplied with 20,000 cubic feet of air per minute.

The furnaces are charged in the following way :—The coke is thrown in by shovelling and distributed as needed, the ore is then charged in from side-tipping cars, the side from which the ore is tipped depending on the position of the charge in the furnace. In order to supply a large volume of air more effectively at the tuyere zone a modified form of tuyere has been introduced. These are 12 inches long by 4 inches wide, and each replaces two of the older $3\frac{1}{4}$-inch tuyeres.

The amount of coke used is about 3 per cent. The matte produced contains from 10 to 12 per cent. of copper, and is resmelted to Bessemer grade in another furnace, the process being that known as the " two stage."

The ore is first smelted with the addition of quartz by pyritic smelting to this low-grade matte, the matte and slag running continuously into settlers 16 feet in diameter, one of which is provided for each furnace. The matte is tapped from the settlers into ladles, from which it is emptied into beds of flue dust in such a manner that the flue dust and matte become incorporated, yielding a material suitable for smelting in the concentrating furnace. The concentration of the matte is effected in one of the smaller furnaces which has been narrowed to 44 inches.

The charge consists of matte with quartz and some limestone, and as much as 800 tons have been smelted in a day. The concentrated matte contains from 30 to 40 per cent. of copper, and is sent to the converters.

At these works the adoption of the " two-stage " process has resulted in less loss of copper and greater profit than in direct smelting to a matte containing 30 to 40 per cent. of copper. The furnace gases are utilized for the manufacture of sulphuric acid.

The resmelting of low-grade matte where it is possible to obtain clean siliceous ores and enough limerock to make a rapid running clean slag, is accomplished with little coke, and at times with remarkable furnace speed. A striking example of both coke and tonnage is the following tonnage which was smelted in a 56-inch by 180-inch furnace in twenty-four hours :—Matte 505 tons, quartz 202 tons, limerock 86 tons, total charge 793 tons. The coke used was 13·5 tons, which is 1·7 per cent. coke on the charge. The furnace took 21,515 cubic feet free air per minute. This is unusual running and low coke. It suggests, however, the ease with which matte may be concentrated and the low cost of the operation. Making a low-grade first matte and resmelting will in many cases make a better copper recovery and result in a greater ore tonnage through the plant than single-stage work, due to the more rapid running of the furnaces when not called on for such a high ratio of concentration (Guess*). The low-grade matte contained from about 13 to 18 per cent. Cu.

After smelting with quartz and a little limestone as before, the resulting matte contained from 30 to 40 per cent. Cu.

The Bessemerizing or "Converting" of Copper Matte.—The process consists in blowing air through molten matte in a suitable vessel called a converter in order to oxidize the iron and some of the sulphur to produce "white metal" or nearly pure Cu_2S, and then by further blowing to oxidize the remaining sulphur, and obtain blister copper.

The converters in which the process is carried out are of two distinct classes, viz. :—

The "acid" converter, and the "basic" converter, as in the Bessemer process for the manufacture of steel. The "acid" converter is so termed as it has a siliceous or "acid" lining, and the "basic" converter because its lining is of magnesite, a basic material.

The acid converter is now being replaced nearly everywhere by the basic-lined vessel.

In each class there are two types, the upright and the horizontal form of vessel.

The Converter with Siliceous or Acid Lining.—Until recent years the acid converter was in universal use, and the type which was employed in almost every converting plant was the horizontal or, as it is sometimes called, the "Bisbee" or the "barrel" converter. The upright converter resembles the ordinary steel converter, except that the blast is admitted through the sides and not at the bottom. This arrangement of the tuyeres is necessary, in order that the blast may not enter below the surface of the reduced copper, otherwise the metal would be oxidized and caused to solidify.

The usual dimensions were—height 16 feet, diameter 8 feet, but at Great Falls the diameter was increased to 12 feet, and in the new basic converter is 20 feet.

The advantages of the upright as compared with the horizontal or barrel converter are :—

(*a*) More rapid oxidation, owing to the greater depth of matte and higher blast pressure.

(*b*) More effective support is given to the lining.

(*c*) The lining is more readily put in.

(*d*) The lining is said to be worn to a lesser extent and more uniformly.

On the other hand, the higher pressure of blast required is a disadvantage.

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* *Eng. and Min. Journ.*, January, 1912.

The Barrel Converter with Siliceous or Acid Lining (Fig. 43).*—Converters of this type were first introduced by Douglas at the Copper Queen Works, Arizona. They were adopted because it seemed unnecessary to continue blowing into a bath of metallic copper as soon as it began to form, which was unavoidable in the old upright converters which were bottom blown. Whereas in the barrel form with tuyeres on one side only the converters can be tilted as the copper is reduced and the blast made to impinge only on the residual unreduced matte. Later forms of the upright converter are, however, side blown. Further, they can be operated with a blast of only 5 to 7 lbs.; at the Washoe plant of the Anaconda Company, however, a pressure of 16 lbs. was found necessary for rapid work.

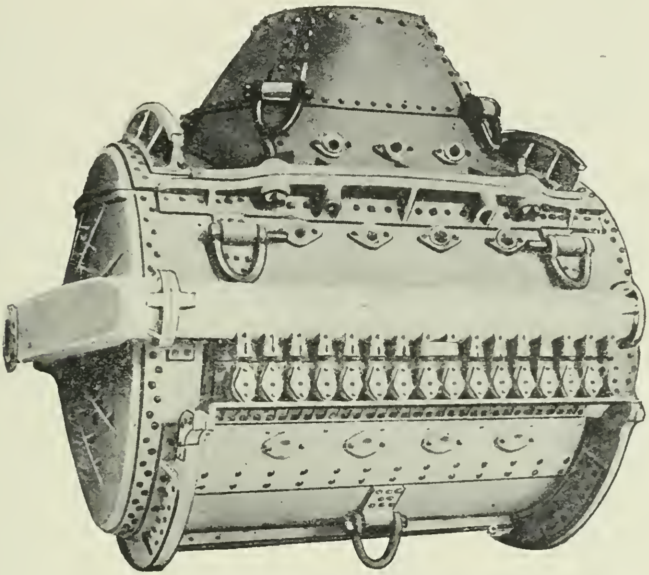

Fig. 43.—Silica-lined Barrel Converter.

This type of converter is a barrel-shaped vessel, and consists of a shell of mild steel or boiler plate $\frac{3}{4}$ inch in thickness, with cast-steel ends, and lined with material containing a high percentage of silica.

It is constructed in two parts, the lower which is the "body" and contains the cavity in which the blowing of the matte takes place, and the upper cover or hood which carries the nose through which the fumes are emitted and the slag and reduced copper poured.

They are held together by bolts, so that they are readily detached for lining and repairs. The blast is led from the blowing engine to a cast-iron horizontal blast box or wind chest which is the length of the shell, and is riveted to it. The tuyeres lead from the blast box to the interior of the converter, and opposite each tuyere there is an opening in the blast box through which a bar can be driven to keep them open.

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* Levy, *op. cit.*, p. 197.

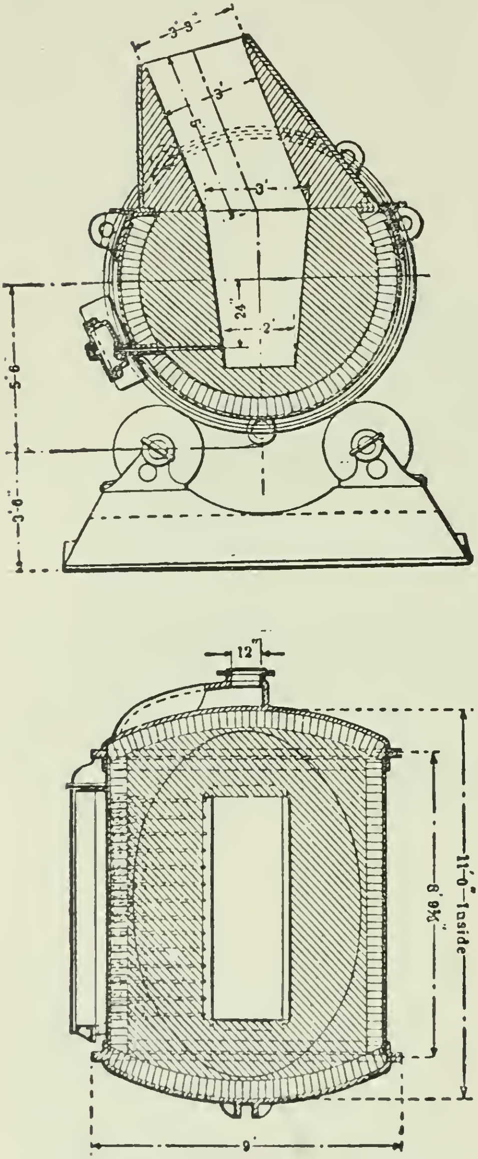

Fig. 44.—Barrel Converter Sections.

The converter is supported on friction wheels set in a strong iron framework known as the stand.

In some of the newest converters the air is supplied from the wind chest to the tuyeres individually, as shown in Fig. 43.

The tilting is effected by means of a pinion, fixed to one end of the shell, gearing into a rack attached to the end of a hydraulic ram. In some cases the tilting is effected by an electric motor.

Barrel converters vary in dimensions from 8 feet by 5 feet to 15 feet by 7 feet. A common size is 10 feet 6 inches in length and 7 feet in diameter, with 12 tuyeres.

At the Washoe plant of the Anaconda Copper Mining Company and at the Tooele Smelter, Utah, the converters were 12 feet 6 inches in length and 8 feet in diameter, and when freshly lined the cavity of the body was 8 feet long, 4 feet wide, and 3 feet 8 inches deep, and of 80 cubic feet capacity. Their average charge was 9 tons, but when nearly worn out they took a charge of 12 to 13 tons.

They had 16 1-inch tuyeres, and the blast pressure was 16 lbs. per square inch. A sectional elevation of a barrel converter is reproduced in Fig. 44, by permission from Dr. Peters' *Practice of Copper Smelting*, p. 484. The air was supplied from piston blowing engines, the pressure varying from 5 to 16 lbs. per square inch at different works.

Lining the Acid Converter.—The material for lining the acid converter must be siliceous, as it has to provide the silica for combining with the iron oxide to form a ferrous silicate slag. The lining is hence rapidly destroyed, having generally to be renewed after only five to eight blows. Various attempts have been made from time to time to introduce silica in the form of sand or siliceous ores in order to save the lining, but in no case would the iron oxide combine with this silica, but only with the silica of the lining. During the last few years, however, by the adoption of basic instead of acid linings this difficulty has been overcome.

When a converter has to be relined it is carried by means of an overhead travelling crane to the lining shop. The upper section is removed and the old lining of the body carefully chipped away. Rods are placed in the tuyere holes. The lower portion of the body is first lined up to about 5 or 6 inches below the tuyeres by tamping in the siliceous material in layers by means of a tamping machine driven by compressed air. A wooden template or mould for the cavity, made in tapered segments to facilitate removal, is then placed in position, and the lining material tamped in between it and the fire-brick lining. The upper section or hood is lined in the same way, but less refractory material is used.

In the case of a new converter a 4-inch course of fire-brick, or, better, of chrome or magnesite brick, is first laid, so that it covers the whole of the interior of the shell, the siliceous lining then being put in as just described.

The lining is dried by a wood fire, followed by a fire of coal or coke, the latter being aided by a gentle blast. When dried the converter is carried back by the crane to the converting department and placed on its stand when it is ready for a charge.

The number of blows that a converter will stand before requiring relining varies generally from five to eight or nine, and depends on the grade of the matte and composition of the lining; but any lining is more rapidly destroyed by a low- than by a high-grade matte owing to the higher percentage of iron it contains.

On account of the rapid destruction of the lining, and to avoid hasty and careless relining, a considerable number of converter shells are required. In many works there are three and in others four for each working stand. The lower the grade of matte treated, the more frequently is relining necessary.

The material usually employed for lining consists of nine parts of coarsely ground quartz with one part of fire-clay ground together in a pug or Chilian mill. But whenever possible siliceous ores containing copper, gold, or silver should be used instead of barren quartz, as those metals then pass into the matte and are obtained in the reduced copper.

The Process of Converting in an Acid-lined Converter.—The grade of matte treated varies at different works, at several a matte containing from 32 to 40 per cent. of copper is converted, but, as a rule, a higher grade matte containing from 40 to 50 per cent. of copper when available will be found to be most suitable.

A certain amount of iron sulphide must be present, as it is the source of heat, hence mattes of higher grade than the last mentioned, either cannot be converted, or give rise to serious difficulties in the operation. On the other hand, very low grade mattes rich in iron, although they give a high temperature, have the serious disadvantages of fluxing the siliceous lining to too great an extent and of producing too much slag.

There are two stages in the converting process :—

1*st Stage.*—The slagging or slag-forming stage, during which all the iron sulphide is oxidized with the formation of a ferrous silicate slag and copper sulphide, and the evolution of SO_2.

The reactions which occur are :—

$$\begin{aligned} 2FeS + 3O_2 &= 2FeO + 2SO_2. \\ 2FeO + 2SiO_2 &= 2FeSiO_3. \end{aligned}$$

The FeS is oxidized at once to FeO, which combines with the SiO_2 of the lining forming a ferrous silicate slag.

No copper is oxidized as long as any iron is present in the charge.

Combining these equations—

$$2FeS + 3O_2 + 2SiO_2 = 2FeSiO_3 + 2SO_2.$$

This reaction is strongly exothermic, and the heat evolved is, according to Richards [*]—

Decomposition of 2FeS	= − 48,000	calories.
Formation of 2FeO	= + 131,400	,,
Union of 2FeO with $2SiO_2$	= + 17,800	,,
Formation of $2SO_2$	= + 138,520	,,
Total	= + 239,720	,,

The heat evolution per kg. FeS = 1,362 calories.

2*nd Stage.*—The reduction period during which white metal, Cu_2S, containing but little iron is converted into blister copper.

In the 2nd stage part of the Cu_2S is oxidized to Cu_2O, and this reacts with more of the Cu_2S to produce metallic copper as follows :—

$$\begin{aligned} 2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2 &= + 185{,}520 \text{ calories.} \\ Cu_2S + 2Cu_2O = 6Cu + SO_2 &= - 38{,}640 \quad ,, \\ & + 146{,}880 \quad ,, \end{aligned}$$

$$3Cu_2S + 3O_2 = 6Cu + 3SO_2 = + 146{,}880 \text{ calories.}$$

Here there is both an exothermic and an endothermic reaction, but the heat evolved is greater than that absorbed, the heat evolution per kg. Cu_2S being 308 calories. The progress of the operations is largely indicated and controlled by the appearance of the flame issuing from the mouth of the converter (see Levy, *Trans. Inst. Min. and Met.*, 1910, p. 117).

As an example of the working of a charge, the procedure practised at the Washoe Works of the Anaconda Company before basic linings were adopted will be described, as it is typical of the best practice followed in converting matte in a siliceous lined converter.

The matte averages 45 per cent. of copper.

The converter when dried is set upon its stand, and a gentle blast turned on for a few minutes to burn the fuel remaining in it.

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[*] Richards, *Metallurgical Calculations*, p. 501.

The matte is brought from the settlers of the blast or reverberatory furnaces in a large ladle by an overhead travelling crane. About 8½ tons of matte are charged in, the converter being in a nearly upright position and the blast at a pressure of 16 lbs. per square inch. A few lumps of coal are thrown in before and during the running in of the matte.

The converter is now turned slightly back, so as to bring the tuyeres more completely under the charge and the blow proper then commences.

During the first part of the blow white fumes, due to the volatilization of zinc and lead, pass out of the mouth of the converter. The flame is red at first, but soon the colour changes, becoming greenish. The green colour becomes more prominent and continues for forty to forty-five minutes. A preliminary pouring off of the slag, now poor in copper, is made to prevent too great an accumulation of slag before the white metal stage is quite reached and to diminish the amount of slag to be resmelted.

The blowing is resumed, and soon the flame assumes a pale blue colour, due probably to copper silicate, which indicates that practically all the iron has been oxidized. The average time up to this stage is one hour.

The converter is now turned and the slag poured from off the white metal into a 5-ton cast-steel ladle until the stream shows signs of "metal." The presence of white metal is detected by holding a rabble in the stream when it appears like spots of grease on the blade.

The slag ladle is taken by the travelling crane and placed in a tilting cradle, by which the slag is poured into moulds on an endless-chain casting machine. The slag contains about 2 per cent. of copper and is smelted in the blast furnaces. When, however, reverberatory smelting is practised, it is taken in the slag ladle whilst molten and poured into reverberatory furnaces.

Some cupriferous scrap, sweepings, and other rich material from the converting operations are now charged into the converter to cool it. The blast is turned on and the converter turned up and the blowing continued until the white metal is converted into metallic copper. The desired temperature of the charge and the amount of sweepings, etc., to be added are determined by the colour of the flame, which should be red brown. If too red, the charge is too cool and coal is thrown in. If too orange, the temperature is too high, and sweepings, etc., are dropped in from a self-dumping bucket. Constant punching of the tuyeres is required during this blow. The time needed for the second blow is from an hour to an hour and a-half.

The end of the blow is difficult to recognize. The indications are :—The shots of copper which are thrown out from the bath no longer stick to the hood of the converter, but rebound from it ; the character of the copper which adheres to the punching rods, and the size and colour of the flame. The first of these is the most important.

When the blow is considered to be finished, the converter is turned down and a small quantity of the copper is poured on to the floor and its appearance noted, if its surface is rugged and uneven the blow is considered satisfactory. The contents of the converter are then poured into a 5- or 10-ton steel ladle lined with fire-clay, and taken by the travelling crane to the refining and casting furnace into which they are emptied.

The final slag which is small in quantity contains about 20 per cent. of copper.

At some works the copper is poured from the converter into an adjustable spoon or small ladle, and thence into iron moulds carried by a platform conveyor moved by hydraulic power, at others into tilting moulds on bogies, by which the ingots can be dropped into a water bosh.

The ingots usually weigh 200 to 300 lbs., but if the copper is rich in gold and silver and intended for sale, they should not much exceed 100 lbs. or be more than 3 inches in thickness.

The methods of casting the copper and the weights of the ingots are the same both in acid and basic converter practice.

When low-grade matte is treated, the charge is blown to white metal, the slag poured off, and a second or even third charge of matte is run in, and the whole blown to white metal before the final blowing to copper, the operation being called "doubling."

The arrangement of the blast furnaces and converters in the old works of the Mond Nickel Company in the Sudbury district, shown in plan and section in Fig. 45,* is a good example of an acid Bessemerizing plant.

The use of acid lining for converters, as already stated, is now generally discontinued, except in a few plants where, owing to special conditions, no economy would result from the change.

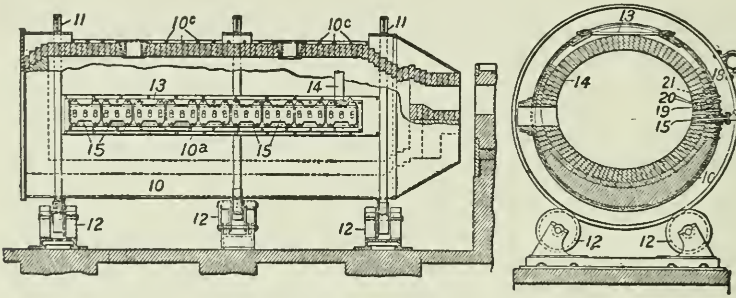

Fig. 46.—Basic-lined Converter.

Converters with Basic Linings.—These converters like those with siliceous linings are of two types, viz.—the horizontal and the vertical or upright.

The basic lined converter, which was the first to be introduced by Messrs. Pierce & Smith, the pioneers of this lining, was of the former type, and several are in use. The vertical type has, however, been found to possess certain advantages, and has been adopted at Great Falls, Anaconda, Cananea, the Copper Queen, and other important copper smelting works.

The horizontal or Pierce-Smith type, which is in use at Garfield and Perth Amboy, is illustrated in Fig. 46.† It consists of a shell of $\frac{3}{4}$-inch steel, 23 feet long and 10 feet in diameter, encircled by three heavy flange rings which rest on friction wheels. The upper part of the shell is left open, the free ends being held together by a series of tie-rods. This is necessary to provide for the expansion of the magnesite lining.

The lining is made of 9-inch magnesite bricks, except at the tuyeres, where 18-inch magnesite slabs are used.

Between this lining and the steel shell is a lining of fire-brick varying

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* *Eng. and Min. Journ.*, August, 1910.

† *Eng. and Min. Journ.*, December, 1910.

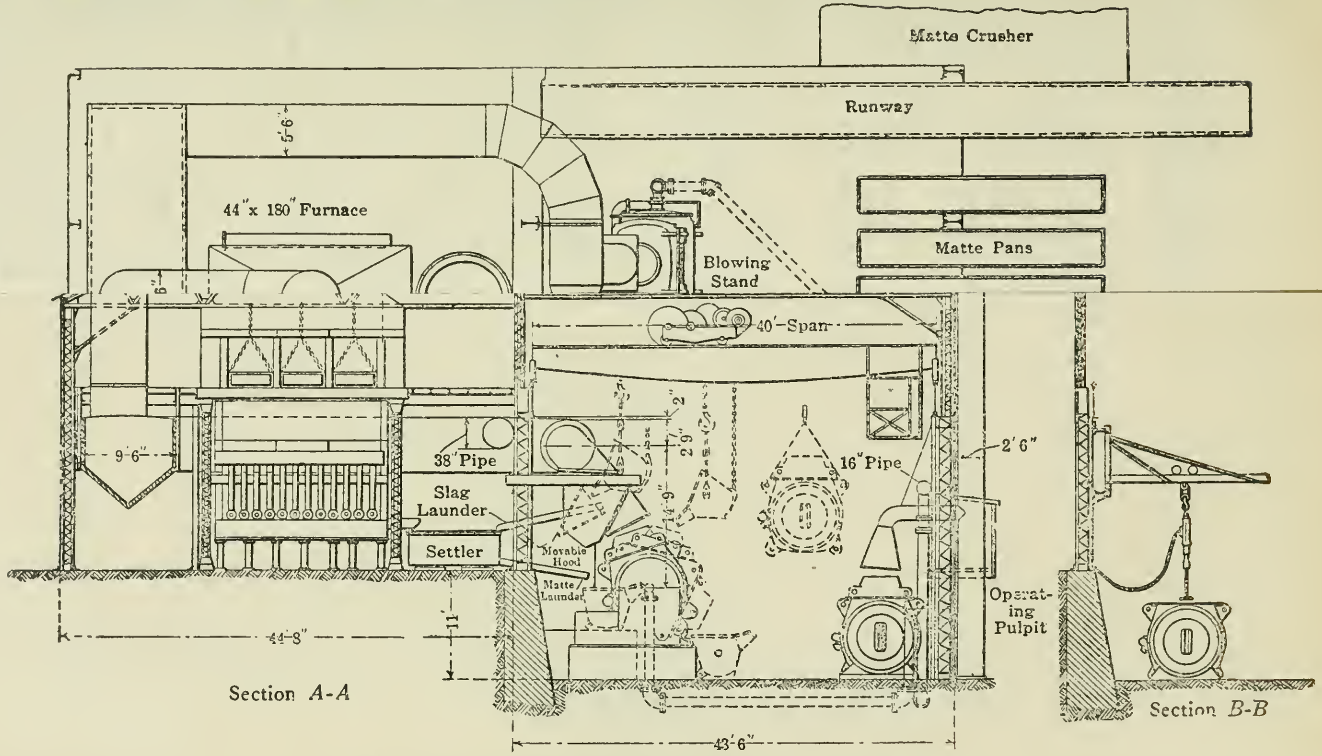
Matte Crusher
Runway
Matte Pans
5'6"
44" x 180" Furnace
Blowing Stand
6"
40'-Span
2"
2'9"
14'9"
2'6"
16" Pipe
9'-6"
38" Pipe
Slag Launder
Settler
Movable Hood
Matte Launder
Operat-ing Pulpit
11'
44'-8"
43'-6"
Section A-A
Section B-B

Fig. 45.—Furnaces and Converters. Mond Nickel Co. (1910).

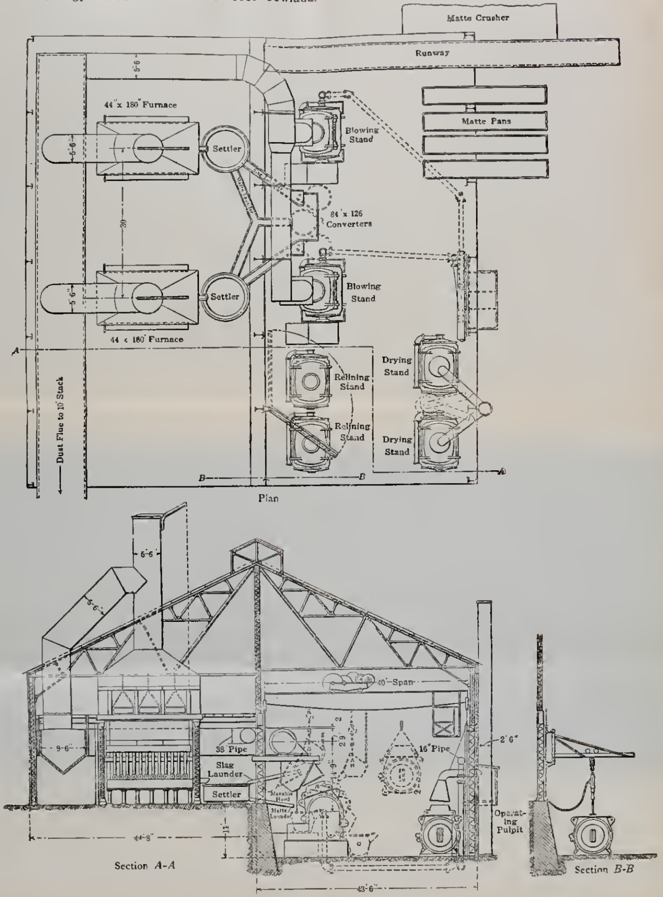
Matte Crusher
Runway
Matte Pans
44" x 180" Furnace
Settler
Blowing Stand
84" x 126 Converters
Settler
Blowing Stand
44 x 180' Furnace
5'6"
5'6"
9'6
30
A
Relining Stand
Relining Stand
Drying Stand
Drying Stand
Dust Flue to 10' Stack
B
B
Plan
6'6"
6'6"
40'-Span
9'6"
38" Pipe
Slag Launder
Settler
Movable Hood
Matte Launder
16" Pipe
2'6"
2'9"
Operating Pulpit
44'8"
11'
43'6"
Section A-A
Section B-B

Fig. 45.—Furnaces and Converters. Mond Nickel Co. (1910).

from 13½ inches in thickness at the bottom to 4 inches at the sides up to about 18 inches below the tuyeres.

The interior after lining is about 20 feet long by 7 feet wide and 6 feet high.

The charging opening or throat is placed at one end. It is circular, about 3 feet 4 inches in diameter, and is surrounded by a cast- or sheet-iron cylinder 2 feet 6 inches high lined with clay or magnesite.

There is an opening in the side opposite the tuyeres for the discharge of the slag and copper, and another in one of the ends for the admission of an oil burner which is used in heating up a new lining and for increasing the temperature of the converter when the copper has cooled too much to pour satisfactorily.

There are 32 1¼-inch tuyeres, each controlled by a valve and separately connected by a flexible tube with the blast box.

The Process of converting in a Pierce-Smith Basic-lined Converter.—The procedure generally is as follows for a matte containing 35 to 40 per cent. of copper :—

The copper from a previous charge having been poured, a charge of four or five ladles of matte (30 to 40 tons) is poured into the converter through the throat and about 3 tons of dried siliceous ore added. The blast is turned on and the converter slowly turned up until the tuyeres are well below the matte. For the first few minutes the pressure of the blast is light, not exceeding about 5 lbs. per square inch. When the ore and matte have become more or less intermingled the pressure is increased to 10 or 12 lbs., and is continued until the silica has been fluxed by the iron oxide, thirty to forty-five minutes being generally required. This is determined by feeling the charge with an iron rod. The converter is now turned down and the slag poured off. Another ladle of matte and the necessary siliceous ore are added and the blowing resumed. These charges are repeated, but with less siliceous ore towards the end, until sufficient white metal has collected to be blown to copper in the usual way.

In the early stages the amount of silica required is determined by the appearance and fracture of small samples of the metal, which are taken out from time to time with a small ladle.

The finish may be approximately determined by the flame, but when lead or arsenic is present this is difficult. The slag is similar in character to that produced in silica-lined converters, but is generally lower in silica. A slag containing 27 per cent. of silica is usually satisfactory.

The wear of the lining is with proper management chiefly confined to a space about 1 foot above and below the tuyeres, and is largely due to the amount of punching required to keep them open. The siliceous ore must be perfectly dried. This is important, as damp ore tends to float on the matte in masses, and then is not readily fluxed by the iron oxides. The necessity for efficient artificial drying is a disadvantage of the process and adds to its cost. On account of the thinner lining and greater conductivity for heat of the magnesite brick, the losses of heat by radiation are much greater than in the acid-lined converter; it is hence necessary to work with much larger charges in order that the required temperature may be maintained.

The advantages of the process are, however, very great, and may be summarized as follows :—

(*a*) The frequent relining necessary with the acid converters is not required, so that the expensive relining plant associated with them is dispensed with, and only a minimum of spare shells is needed.

(*b*) The vessels can be made larger as they can be relined *in situ.*

(*c*) Lower grade mattes can be treated at less cost than in an acid converter.

(*d*) Siliceous ores containing copper, gold, and silver, which are unsuitable for lining acid converters, can be used and have their metals extracted.

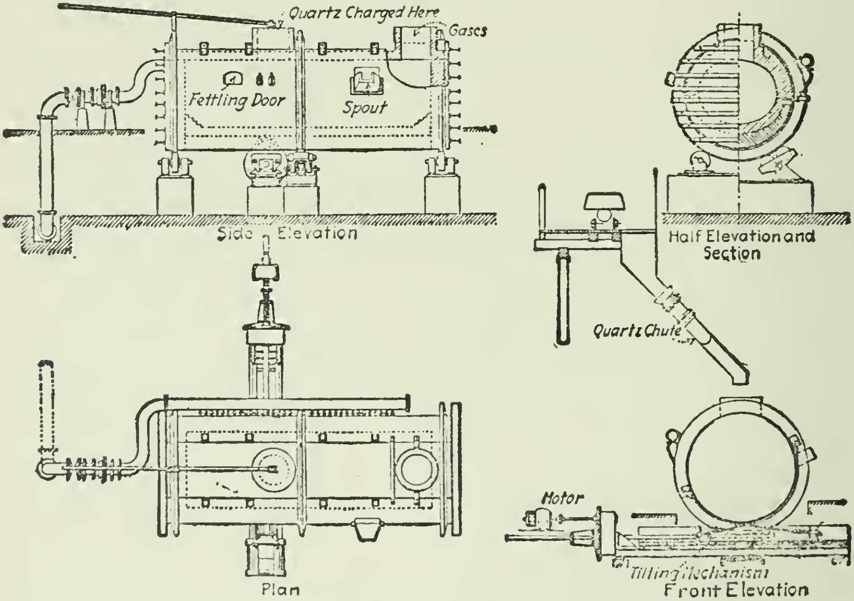
Quartz Charged Here
Gases
Fettling Door
Spout
Side Elevation
Half Elevation and Section
Quartz Chute
Plan
Motor
Tilting Mechanism
Front Elevation

Fig. 47, *a*, *b*, *c*, *d*.—Basic-lined Converter, Karabash Smeltery.

The disadvantages are :—

(*a*) The great care required in working the converter, otherwise there may be rapid destruction of the lining.

(*b*) Losses due to the blowing out of the dry ore.

(*c*) The excessive amount of tuyere punching required, causing destruction of the lining near the tuyeres.

(*d*) Its inapplicability to converters of very small size, owing to the inability to properly control the temperature of the charge, and the resulting destruction of the lining (Howard).

The advantages, however, largely exceed the disadvantages.

At Kyshtim in the Urals,* at the Karabash smelter there are two basic-lined converters of the Pierce-Smith type (Fig. 47, *a*, *b*, *c*, *d*). The shells are 25 feet 10 inches long by 10 feet diameter lined with magnesite brick. For feeding quartz a special opening was made in the top of the converters close to the central riding ring. When the blast is on, this opening is closed by a heavy cover. The advantage of this opening is that it permits quartz or siliceous ore to be charged whilst matte is poured in at the opening at the end, and thus time is saved.

Another alteration was to cut a second opening in the front side of the shell in order to facilitate fettling.

At first the conversion of matte containing only 20 per cent. of copper was followed, but this resulted in rapid deterioration of the lining. The extremely high temperature could not be kept down by adding scrap and excess of quartz, and the slags would frequently contain only 18 or 20 per cent. of silica. At the temperature of formation of such slags, the bricks at the tuyere line were rapidly destroyed by the abrasive and corrosive action of the bath. Mattes containing from 30 to 40 per cent. of copper are now used, the results being that there are no rapid corrosion of the linings and no difficulty in keeping the amount of silica in the slags up to 25 per cent. or higher.

(At Kalala, however, on the east of the Urals, poor matte containing from 11·8 to 19·3 per cent. copper is regularly blown to copper in 12-foot upright basic converters (see also p. 132).†

The matte is charged from ladles carried by a travelling crane, and the quartz through a shoot from cars on the furnace charge floor level.

The operations are as follows :—" When the copper of a previous blow has been poured the converter is fettled, if necessary, with magnesite mixture (ground magnesite and sodium silicate solution) ; from four to six ladles of matte are then charged, and at the same time sufficient quartz to make a good slag. When this is formed it is poured, another ladle of the matte and more quartz added, and so on, the matte being gradually concentrated until there is a sufficiently large bath of white metal to finish. When a blow is finished the copper is transferred by the crane in 5-ton ladles to a casting machine of the endless conveyor type.

By tilting the ladle the copper is poured into the moulds as they are carried in front of it on the endless conveyor. The copper chills rapidly enough to fall out easily as the moulds pass over the sprocket wheels at the delivery end of the machine. The bars are then trimmed and sent to the refinery. The slags are received in ladles, carried by the crane, and poured through launders into the blast-furnace settlers.

The advantages claimed for the upright as compared with the horizontal or barrel converter have been already stated on p. 118.

Upright Basic Converters.—At Great Falls an upright basic converter of the following dimensions was blown in—20 feet diameter inside the shell and 17 feet high.

The lining is of magnesite brick 2 feet 6 inches thick on the tuyere side and 2 feet thick on the opposite side. There are 62 tuyeres $1\frac{3}{4}$ inches in diameter, and the air consumption is 25,000 cubic feet per minute.

This converter is illustrated in Fig. 49.‡

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* Ernest J. Carlyle, *Eng. and Min. Journ.*, June, 1912.

† *Mining and Scientific Press*, Sept. 1917. ‡ *Mining and Scientific Press*, Oct. 1912.

The following is a summary of the working of a charge (1912) :—*

Initial charge of matte, 65 tons.
Air, 25,000 cubic feet per minute.
Air pressure, 6 to 12 lbs.
Actual time of blowing, 5 hours 19 minutes.
Total time, including charging, etc., 7 hours 23 minutes.
Copper cast, 52·3 tons.
Copper cast per 24 hours, 170 tons.

"The output of the converter, in February and March, 1914, averaged daily 92·2 tons of copper upon a 35·1 per cent. copper matte, and using 71·3 tons of siliceous flux." †

At Anaconda the old 12-foot acid converters which had been lined with basic material have been replaced by large upright basic converters of the Great Falls type, measuring 21 feet in diameter.

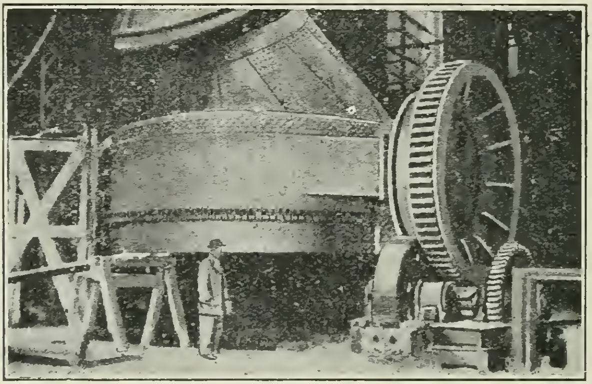

Fig. 49.—Upright Converter, Great Falls Smelter.

Each converter is furnished with a 100 H.P. motor, and can be completely revolved on its horizontal axis.

Air is supplied through 31 independent tuyeres of 1¾ inches diameter.

In Fig. 48 ‡ is given a section of the converter building, showing the position of the converter, the goose-neck flue, the dust chamber, and the track carrying the 20-ton matte car.

There are, however, but few plants that can keep a 20-foot converter constantly in operation, though according to E. P. Mathewson this size is superior to the 12-foot converter in easy handling and temperature control.

We hence find the 12-foot converter installed at most works, and all of the Great Falls upright type. For example, there have been 7 at Copper Queen,

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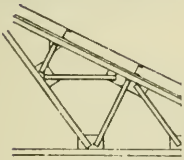
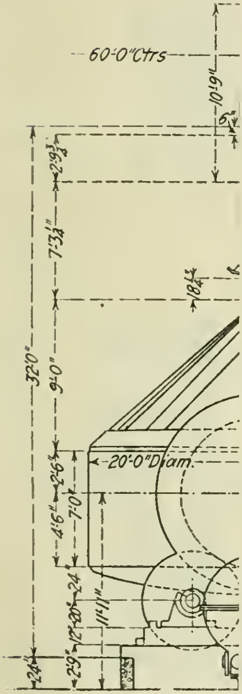
* *Mining and Scientific Press*, January, 1913.
† *Mineral Industry*, 1915, p. 223.
‡ *Eng. and Min. Journ.*, June, 1914.




60'-0" Ctrs
10'9"
6½"
2'9¾"
7'3¼"
18¼"
32'0"
9'0"
2'6"
20'-0" Diam.
4'6"
7'0"
24
11'11"
20"
12"
2'9"
24"

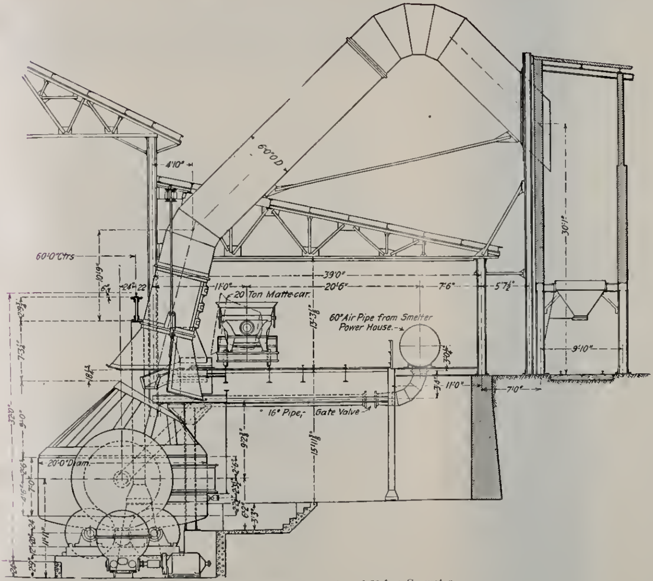

6'0"D
4'10"
60'0"Ctrs
10'9"
6½"
24"
22
11'0"
20 Ton Matte car
39'0"
20'6"
7'6"
5'7½"
13'3⅞"
60" Air Pipe from Smelter Power House
3'0¼"
30'1"
9'10"
2'9½"
7'3½"
18½"
3'4"
11'0"
7'0"
16" Pipe
Gate Valve
9'2⅞"
15'11⅞"
32'0"
9'0"
20'0" Diam.
7'0"

Fig. 48.—Anaconda Elevation of 20-foot Converter.

Arizona; 7 at Cananea, Mexico; 6 at the Calumet and Arizona plant, Arizona; 5 at Miami, Arizona; 2 at the Granby plant, Grand Falls, B C, besides those at several other important works.

One of those at the Granby plants is illustrated in Fig. 50.*

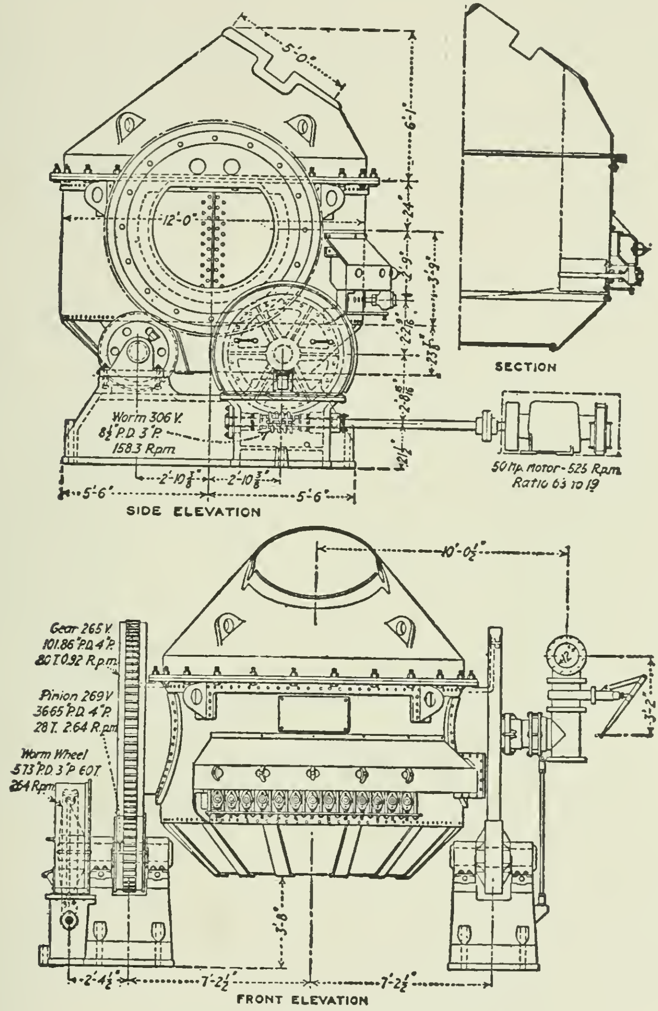

5'-0"
6'-1"
12'-0"
24"
2'-9"
3'-9"
2'-2 7/16"
2'-3 5/8"
2'-8 5/16"
21 1/2"
Worm 306 V.
8 1/2" P.D. 3" P.
158.3 Rpm.
2'-10 7/8"
2'-10 3/8"
5'-6"
5'-6"
SIDE ELEVATION
SECTION
50 hp. motor - 525 Rpm.
Ratio 63 to 19
10'-0 1/2"
Gear 265 V.
101.86" P.D. 4" P.
80 T. 0.92 R.p.m.
Pinion 269 V
36.65" P.D. 4" P.
28 T. 2.64 R.p.m.
Worm Wheel
57.3" P.D. 3" P 60 T.
2.64 Rpm.
3'-2"
3'-8"
2'-4 1/2"
7'-2 1/2"
7'-2 1/2"
FRONT ELEVATION

Fig. 50.—New Granby 12-foot Converter.

In the upright basic 12-feet converter the average charge will range from 34 to 40 tons of matte, containing from about 28 to 35 per cent. Cu. The number of tuyeres ranges from 24 to 28, usually of $1\frac{1}{4}$ to $1\frac{1}{2}$ inches diameter, but in that illustrated there are only 13, but they are 2 inches in diameter. The blast pressure is 12 to 14 lbs.

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* *Eng. and Min. Journ.*, June, 1914.

The method of lining at Cananea is shown in Fig. 51.*

A 3-inch expansion joint is left at the top of the lining of the cylindrical portion of the converter, and the dry, ground magnesite and clay in the space in the half-circle of the body, opposite the tuyeres, is filled in loosely to allow for expansion. In lining, it is important to use as little water as possible for the reason that the magnesite bricks are liable to absorb moisture and disintegrate when a moderately high temperature is attained. Of course, care must be used in the storing of magnesite bricks, as this expensive product may readily be rendered worse than useless by absorbing moisture and later disintegrating after the bricks are in place.

In order to protect the magnesite lining, Wheeler and Krejci † have introduced a method of coating it with magnetic oxide of iron. A newly lined converter is first brought to a bright red heat, then charged with liquid low-grade matte without adding the usual siliceous material, and blown for 10 to 15 minutes, cold matte being then added to reduce the temperature. The charge is alternately blown and cooled until it has been converted to white metal, which is poured. The bricks will then be found to be coated with magnetite. Fresh charges with a little siliceous material are then blown successively, until the coating of magnetite is sufficiently thick and all joints of the brickwork have disappeared.

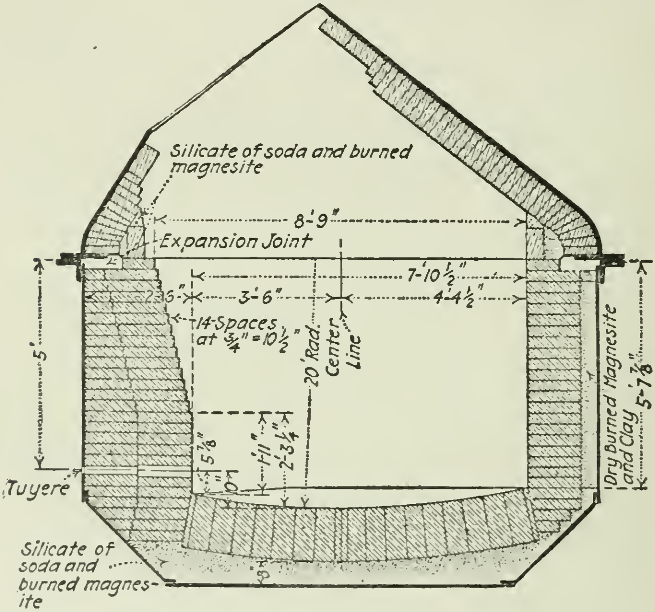
Silicate of soda and burned magnesite
8'-9"
Expansion Joint
7'-10½"
2'-3"
3'-6"
4'-4½"
14 Spaces at ¾" = 10½"
20' Rad.
Center Line
5'
5⅞"
1'-11"
2'-3¼"
10"
Tuyere
Dry Burned Magnesite and Clay
5'-7⅞"
Silicate of soda and burned magnesite
9"

Fig. 51.—Lining of Upright Basic Converter.

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* *Ibid.*, April, 1914.

† *Bull. A.I.M.E.*, February, 1914.

A basic lining should last for 20,000 tons of matte, but this is often greatly exceeded.

One of the most successful runs in any converter is that at the Old Dominion smelter at Globe, particulars of which are as under, according to L. O. Howard :—*

Began operation,	June 27, 1913
Removed for initial patching,	December 7, 1915
Number of blows made,	3,288
Time of blow, hours,	4·18
Matte charged, tons,	85,578
Copper content of matte per cent.,	43·37
Bullion produced, tons,	35,431
Copper per blow, tons,	10·80
Blast pressure, lbs.,	13·2
Air used per minute, cubic feet,	7,691
Ore fed, tons,	17,097

The working of a charge in a 12-foot basic converter is described by Hofman, as follows :—†

"In starting a newly lined converter—*e.g.*, the 12-foot—the lining is dried and warmed with a wood fire for 36 to 48 hours; the ashes are removed, and two ladles or 16 tons of matte (Cu 35 per cent.) poured in; the vessel is turned over, blown 2 to 3 minutes, and turned down to see the effect the blow has had on the brick lining. This operation is continued with additions of fresh liquid matte and with extensions of the duration of the blows until the cracks between the bricks have been filled, and the surfaces so coated that the individual bricks cannot be recognized, the remaining matte is poured off, and the converter left undisturbed for a few hours to harden the matte in the crevices and the coating on the outside of the brick.

"The vessel is now ready for normal work. In this there are charged two ladles or 16 tons of liquid matte, then 3,700 lbs. siliceous ore (Cu 3·5, SiO_2 57·8, FeO 13·0, Al_2O_3 11·0, CaO 0·1, S 12·1 per cent.); the blast is started, the vessel turned over and blown for 30 to 40 minutes, with a pressure of 14 lbs.; the slag formed is poured off. There is now poured in one ladle or 8 tons of matte and shot in 1,800 to 3,700 lbs. of ore, depending upon the grade of the matte, followed by 1·0 to 2·5 tons of converter cleanings and cold matte, all of which reduce the temperature of the bath; the vessel is again blown and skimmed. The operations are repeated until five or six ladles of liquid furnace matte have been introduced, and the converter matte has been brought forward to near the white-metal stage (Cu 70 to 75 per cent., recognised by its behaviour on the rabble); the slag formed is poured off as much as possible and the rest skimmed; "dope" are fed in the form of scrap copper, white metal, and cleanings, which reduce the temperature of the bath, which is now blown to a finish in 5 to 6 minutes for every ton of copper in the vessel (12 to 14 tons of Cu or 18 tons of white metal).

"The tuyeres are punched more or less continually, less so during the slagging than the blister stage.

"The progress in the process is usually judged by the flame; when in doubt, the vessel is turned down and the matte examined, or the copper is tested on the rod.

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* *Min. and Sc. Press.*, September, 1916.

† Hofman, *Metallurgy of Copper*, p. 352.

"The actual blowing time is 20 minutes per ton of copper produced; a charge with matte of 38·9 per cent. Cu takes 8·5 tons of ore, or 0·7 ton of ore per ton of Cu; the charge produces 12 to 14 tons of Cu.

"The converter copper is poured into ladles and transferred to a copper-casting machine. The converter slag (SiO_2 19·7, FeO 60·7, Al_2O_3 6·3, CaO 1·3, MgO 0·25, Cu 1·6 to 2·0, S 2·0 per cent.) is also poured into a ladle and handled in a slag-casting machine."

At Anaconda the molten converter slag is taken to the large coal-dust-fired reverberatory furnace already mentioned (p. 93), where it is smelted with raw sulphide ore to recover the copper it contains.

At the Granby Smelting Works at Anyox, B.C., low-grade matte was formerly concentrated to converter grade by resmelting with quartz. Two 20-foot converters of Great Falls type have been erected and are now in operation, converting all the matte of whatever grade direct to copper. It is hoped, however, to keep the grade at 16 per cent. Cu.

The converters, one of which is shown in Fig. 51*a*, are of special construction.

Experience has shown that with converters of the usual design there is a tendency to sag after operating, thus throwing the gears out of line. To obviate this, the new type of converter has been reinforced with cast angle plates and a ribbed top. These additions insure a stiff beam effect; but, in order to compensate for any possible sagging, the gears have been designed slightly bevelled, so that when the sag does develop it will straighten up.*

Losses in the Converting Process.—When mattes of average content of copper and silver are treated in the converter, the loss of copper will be about 1·0 to 1·5 per cent., and of silver 2·0 to 2·5 per cent.

In the basic converter the loss of copper is small, as the percentage of Cu in the slag is low; in fact, 95 per cent. of the Cu in the matte is recovered as blister copper compared with 65 per cent. in the acid converter (Hofman).†

As regards the elimination of impurities in the basic converter no data are available, but it should not differ much from that obtained in the acid converter. When the mattes contain zinc or much lead, the loss of silver is very much greater, but a considerable amount may be recovered if there is a bag-house.

The chief loss of silver occurs in the final stages of the operation.

Elimination of Impurities.—The extent to which impurities are removed in the process of converting has been investigated chiefly by Keller, Gibb, and Mathewson. The results obtained by them respectively have been communicated to the American Institute of Mining Engineers, and are published in Volumes xxviii., xxxii., and xxxviii. of the *Transactions*, to which the student is referred for details.

The degree of elimination of any one of the impurities appears generally to depend, not only on the percentage present in a matte, but also on the amounts of the other impurities which occur with it. The metals which are fairly easily oxidized, as iron, cobalt, zinc, and lead, are removed on an average to the extent of 99 per cent. of the three first, and 96 per cent. of the last. Parts of the zinc and lead are volatilized.

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* W. A. Williams, *Eng. and Min. Journ.*, 1919, p. 980.

† Hofman, *Metallurgy of Copper*, p. 343.

As regards the other impurities, Peters states—" Bismuth is removed in a highly satisfactory manner by the converter, being driven off mainly by volatilization. Experiments show that 94 to 96 per cent. of this injurious element is removed in this manner.

" Arsenic is volatilized to the extent of from 70 to 90 per cent., one-half of it, or more, being driven off during the first thirty minutes of the blow. Antimony is less satisfactory, losing 60 to 73 per cent. Selenium and tellurium are removed to about the same extent as antimony." *

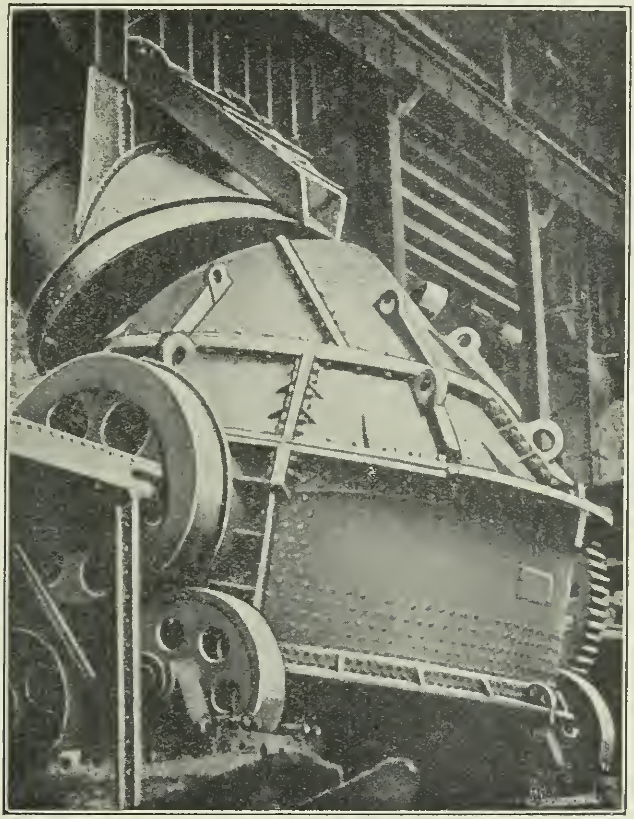

Fig. 51*a*.—Converter at Granby Smelting Works.

Examples of Copper Smelting Practice.—The following accounts are supplementary to the information given in the foregoing pages :—

Arizona Copper Company, Clifton, Arizona—Reverberatory Smelting Works.—The following description is abstracted from accounts of the works by

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* Peters, *Practice of Copper Smelting*, p. 530.

F. N. Flynn,* and by R. H. Vail.† The works is a reverberatory smelting plant, no blast furnace having been erected, though space has been reserved for a blast furnace department should it be required later. The major portion of the copper production is from the concentrate obtained from so-called "porphyry" ores. The "bedding" system is adopted for the concentrate, whilst only part of the coarse ore is bedded and part sent to storage bins.

The roaster equipment consists of eight Herreshoff furnaces, 21 feet 7 inches in internal diameter, heat being supplied to each furnace by two external fires. Each furnace has an output of from 60 to 80 tons of calcine (roasted material) per day. The gases leaving the furnaces first enter a hopper-bottomed flue and then pass into a large dust chamber. This chamber is 180 feet long by 48 feet broad, with a cross-section of 1,325 square feet, and having steel wires suspended in it hung at 4-inch centres from $\frac{3}{8}$-inch chains.

There are three reverberatory furnaces for the production of matte, either one or two being worked as required, and one being kept in reserve. The furnaces have a hearth area of 100 feet by 22 feet, and are arranged side by side 26 feet apart. The fettling is done through 6-inch holes left in the roof along the side walls and across the back. Above there are trough-shaped hopper bins, from which the fettling material is fed through 8-inch pipes.

Two parallel charge tracks cross the furnaces near the back in a direction at right angles to their length. Charges of 15 tons of hot calcine are dropped through one water-jacketed charge-hole in the centre of the roof on either track, but 90 per cent. of these charges are dropped from the back track. Of the total solid charge smelted, 75 per cent. is introduced in this way. The remaining 25 per cent. consists of ore and by-products crushed to $2\frac{1}{2}$-inch size fed in as fettling through the fettling holes, and containing 6 per cent. Cu. The coarse fettling is fed up to the holes in the roof, and is said to be more effective than when more finely ground.

The furnaces are oil-fired. Steam is raised in seven Stirling boilers, each of 712 H.P., so placed in the flues that they are heated by the hot gases from all the furnaces.

The matte contains about 37 per cent. Cu, and is taken in 20-ton cast-steel ladles to the converter department.

The capacity of a furnace when smelting roasted concentrate containing 14·1 per cent. Cu averaged 365 tons per day.

In the converter department there are three converter stands, a fourth being under construction, and five 12-foot converters of the Great Falls' upright type, lined with magnesite bricks. The pressure of blast is 13 lbs. Siliceous ore containing SiO_2 65 per cent., Al_2O_3 11 per cent., and Cu about 6 per cent., is used as flux, a small quantity of siliceous material containing SiO_2 80 per cent. being added near the end of a blow. The average time of blowing a charge is four hours, the blister produced averaging from $6\frac{1}{2}$ to 8 tons. The shells are coated with magnetic oxide of iron (see p. 130), when the lines of brickwork can be seen through the old coating.

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* Excerpt from a paper read at the Arizona meeting of the A.I.M.E., by F. N. Flynn, *Eng. and Min. Journ.*, October 14th, 1916.

† *Eng. and Min. Journ.*, June 27th, 1916.

The gases from the converters pass into a dust chamber 130 feet long by 25 feet wide, with a cross-sectional area of 500 square feet. The chamber is provided with suspended wires, as in the dust chamber of the roasting department.

The copper is transferred from the converters to casting machines in cast-steel ladles. The bars are cast in moulds made of converter copper, and weigh 240 lbs. each. The converter slag is taken in ladles to the smelting department, where it is poured through the back wall of one of the furnaces by means of a launder discharging at the height of the oil burners.

*The Copper Queen, Douglas, Arizona—Smelting in Blast Furnaces and Reverberatories.**—The average composition of the ore treated by the plant in 1915 was in percentages—Cu 9·13, SiO_2 56·0, Fe 8·10, CaO 1·0, Al_2O_3 8·4, S 6·1, with Au 0·075 oz. and Ag 3·46 ozs. per ton.

The ores, after being through the sampling mill, are bedded in five rock-walled pits or beds, each 750 feet long, 38 feet wide, and 11 feet deep, converter slag and other fluxes being added, so as to form a mixture suitable for smelting. The cars for charging the blast furnace are filled from these beds by steam shovels, are then taken to the coke-box, where each receives a weighed quantity of coke, amounting to about 12·4 per cent. of the charges, and thence to the charging floor of the blast furnaces. The furnaces are charged by simply tilting the cars.

There are 10 blast furnaces, 44 inches wide at the tuyeres, 5 being 18 feet, and the others 20 feet long. The tuyeres are 4 inches in diameter, spaced 12 inches apart, two being served by one blast pipe. The blast pressure is about 28 ozs. The gases pass through downtakes 8 feet in diameter to a capacious dust chamber fitted with suspended wires. The furnaces have oval settlers, 20 feet by 12 feet and 23 feet by 10 feet, set at right angles to their long axes.

In 1915 the average charge smelted per furnace per day was 374·8 tons, the matte produced averaging 35·06 per cent. Cu.

In the roasting department there were 16 MacDougall six-hearth roasters, 18 feet in diameter. The material roasted consisted of 55 per cent. concentrate and 45 per cent. crushed ore, no fuel being required except a little oil on starting. The dust produced is collected in a dust chamber, 42 feet wide by 144 feet long, with a sectional area of 1,200 square feet fitted with suspended wires. The average daily output of roasted ore was 475 tons per furnace. The reverberatory smelting department contains three reverberatory furnaces, with hearths 91½ feet long by 19 feet wide, each of which raises steam in two water-tube boilers of 520 H.P. placed in the flue. The material smelted consists chiefly of calcines with some flue dust and the ore used for fettling. The fettling for the sides and bridge is dropped through holes in the roof. Oil is used as fuel for firing the furnaces. According to the latest returns (1915) the average amount of charge smelted per furnace was 338·7 tons per day, the matte produced being somewhat richer in copper than that from the blast furnaces.

A dust chamber is also provided for the gases from the department.

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* Vail, *Eng. and Min. Journ.*, January, 1915; editor *Eng. and Min. Journ.*, April and October, 1916.

In the converting department there are nine stands for basic converters of the 12-foot upright type but with concentric mouths.

The matte from the blast furnaces and the reverberatories is brought to the department in large ladles in the usual way. In starting a converter, the matte of the first ladle or more is blown without silica to form a coating of magnetic oxide of iron on the magnesite lining.

During 1915 the average daily production per stand was 32·6 tons of copper, an average of 8·3 stands being operated. The blast pressure employed was 13 lbs. per square inch.

The converter slag is used as flux for the blast furnace charges. To that end it is hauled to the tracks alongside the ore beds, and as the motor moves along the bed, the slag-pot is slowly tilted, so that its contents are spread over the ore in a thin layer.

The copper from the converters is taken in ladles by an electric travelling crane to the pouring stands of two Walker casting machines, where it is cast into bars. The average composition of the bars is Cu 99·2 per cent., with Au 0·387 and Ag 19·47 ozs. per ton.

*The Calumet and Arizona Smelter.**—The ore smelted is of two classes, one which is very siliceous contains approximately 4 per cent. copper, present mainly as carbonate and silicate. This is used as reverberatory fettling and as a flux for the converter charges. The other, which is the main supply of ore, averages about 5 per cent. copper, 18 per cent. silica, and 28 per cent. sulphur. The roasting plant consists of 24 Herreshoff furnaces, each being 20 feet 2 inches internal diameter, and having six hearths exclusive of the drying pan. In the smelting plant there are four oil-fired reverberatory furnaces, each 20 feet by 100 feet, and two blast furnaces of the Mathewson type 40 feet long by 4 feet wide at the tuyere-section.

In the converter plant there are six 12-foot basic-lined converters of the Great Falls type. A plan of the smelter is shown in Fig. 52.

The ore is crushed to 4-inch size, the coarser sulphide being sent to the mixing beds for the blast furnaces, while the remainder is brought down to approximately ½-inch size for the reverberatory furnaces. The sulphides go to the Herreshoff furnaces to be roasted, and the oxide ores direct to the charging bins. Five of the roasters are running " closed," the gases being sent through flues and a dust chamber to the sulphuric acid works ; the remaining nineteen are running " open," the gases pressing through a dust-chamber 140 feet long and 60 feet by 29½ feet in vertical section, on their way to the stack. The calcined ore from the open furnaces contains about 10 per cent. sulphur, as against 13 per cent. from those connected to the acid plant. The capacities of the " open " and the " closed " furnaces are respectively 90 and 70 tons each per day. In each of the two blast furnaces there are 64 tuyeres, 4½ inches diameter, and the elevation from the tuyere-line to the feed-floor is 16 feet 4½ inches. The blast is supplied at a pressure of 27 ozs., and the coke used is 12·7 per cent. The average charge contains 5·29 per cent. Cu, and the matte produced 28·81 per cent. Cu.

Each reverberatory furnace is erected upon a deep foundation of poured slag. Upon this is a 4-inch layer of tamped fire-clay followed by 12 inches of crushed quartz under the matte-bay and 21 inches under the remainder

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* Courtney de Kalb, *Mining and Scientific Press*, August, 1918.

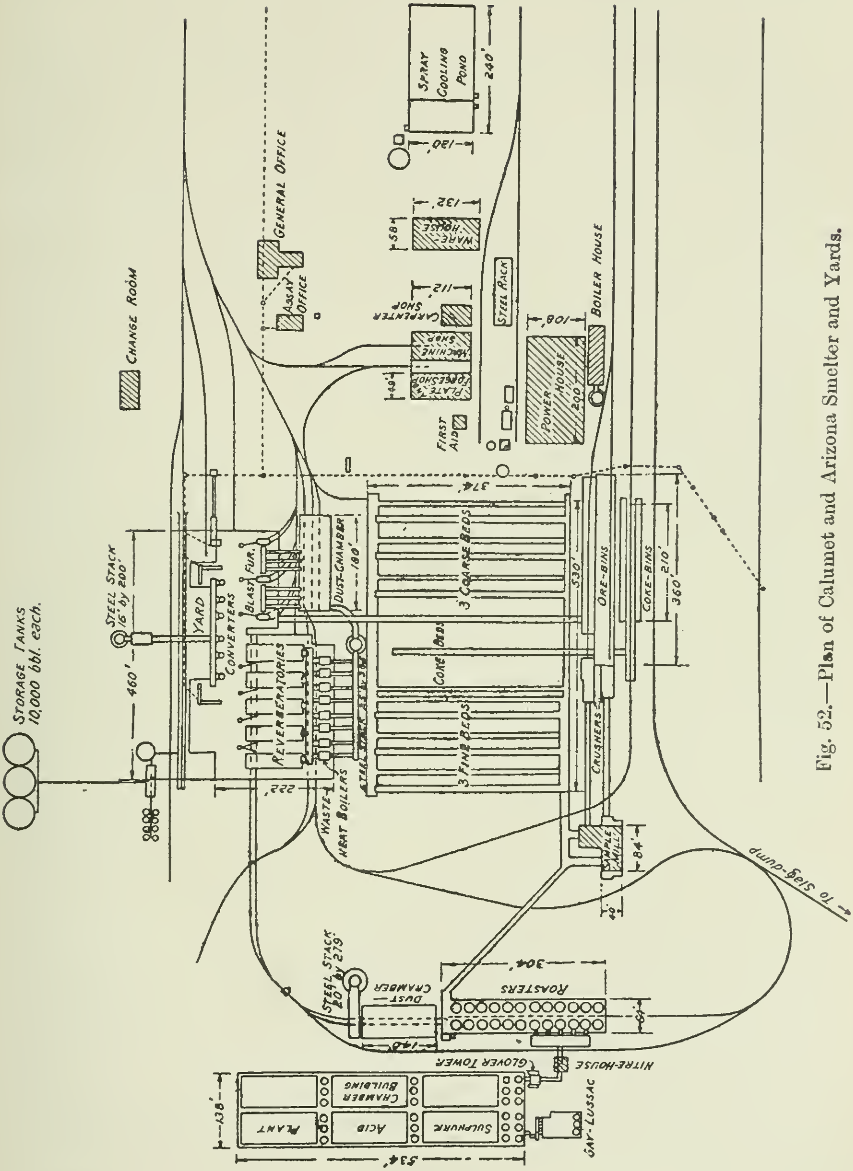
STORAGE TANKS 10,000 bbl. each.
STEEL STACK 16' by 200'
460'
YARD
CONVERTERS
BLAST FUR.
REVERBERATORIES
DUST-CHAMBER
180'
STEEL STACK
222'
WASTE-HEAT BOILERS
CHANGE ROOM
GENERAL OFFICE
ASSAY OFFICE
CARPENTER SHOP
112'
MACHINE SHOP
PLATE & FORGESHOP
49'
FIRST AID
WARE-HOUSE
58'
132'
130'
SPRAY COOLING POND
240'
STEEL RACK
108'
BOILER HOUSE
POWER HOUSE 200'
374'
3 COARSE BEDS
COKE BEDS
3 FINE BEDS
530'
ORE-BINS
COKE-BINS
210'
360'
CRUSHERS
SAMPLE MILL
84'
To Slag-dump
STEEL STACK 20' by 279'
DUST CHAMBER
140'
304'
ROASTERS
GLOVER TOWER
NITRE-HOUSE
GAY-LUSSAC
SULPHURIC ACID PLANT
CHAMBER BUILDING
138'
534'

Fig. 52.—Plan of Calumet and Arizona Smelter and Yards.

of the furnace hearth, the matte-bay being 20 feet long. There are 42 holes for fettling and charging on each side, 6 inches by 6 inches in size, and spaced 2 feet apart from centre to centre, open through the arch close to the inner wall.

The side-feeding of both fettling and ore high along the walls as adopted here has been found more advantageous to the working of the furnaces than the method of feeding the ore through ports in the middle of the roof and the fettling only through the ports at the side, as a more uniform state of the bath can be maintained. The output of each furnace has also been increased, formerly only 400 tons, exclusive of converter slag, were treated daily, but now 700 tons are treated. This increase in smelting capacity is attributed to a more intense combustion of the fuel oil close to the firing end, which limits the smelting zone to approximately the same limits. The charging is hence not carried so far to the front of the furnace, leaving the remainder of the hearth to constitute a pool, in which the matte separates more completely from the slag.

The copper in the reverberatory charge ranges from 5·16 to 5·40 per cent., and in the matte is about 25 per cent.

The average consumption of oil burned per ton of total charge is 0·719 barrel, which, after deducting 0·303 for the credit of steam, leaves the net consumption chargeable against the ore smelted of 0·416 barrel.

In the converter department there are six converter stands, mounting 12-foot basic-lined converters of the Great Falls type. Two extra shells are kept on hand to facilitate repairs. The siliceous ore is fed into the converters through pipes leading from overhead bins.

The matte is blown to blister containing on an average 99·15 per cent. copper. It is cast into ingots of 300 lbs. each, being poured from 160 cubic foot cast steel ladles into moulds in a straight-line casting machine.

Smelting Copper Concentrate in Blast Furnaces after Nodulizing and Sintering—*The Braden Copper Company, Chile.**—The plant treats 350 tons of concentrate daily, which has been obtained by the treatment of 4,000 tons of ore. The dry concentrate consists of 19 per cent. Cu, 17 per cent. SiO_2, 23 per cent. Fe, 2 per cent. CaO, 8 per cent. Al_2O_3, 28 per cent. S. It is sandy and slimy, and contains 20 per cent. H_2O as received.

Of the 350 tons of concentrate, about 215 tons is sent to the nodulizing kilns. The kilns are of the revolving cylinder type, and are heated by oil burners to a temperature of 950° C. In the kilns the concentrate is quickly heated by the burning of the oil and also by the combustion of a part of the sulphur to a sticky consistence in which state the rolling motion tends to ball it into nodules of varying size. The kilns are sloped an inch per foot towards the discharge end, out of which the red-hot nodules pour on to an endless chain of cast-iron pans, which convey the product to the blast furnaces. In the process of nodulization the proportion of sulphur has been reduced from 28 to 18 per cent.

Another 50 tons of the concentrate is sent to the sinter plant of four units. Each unit is a concrete box 4 feet wide by 50 feet long, covered with a perforated cast-iron plate. An exhaust fan is connected to the box, creating a strong down-draught of air through the grate. A 4-inch layer of concentrate is spread on the grate with an inch layer of sawdust ignited with kerosene torches after the fan has been started. The sawdust starts the combustion of the sulphur in the concentrate.

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* *Mining and Scientific Press*, Feb. 1916.

The roasting continues for an hour, when the sulphur is reduced to 12 per cent., and the loose layers are converted into hard cake. The cake is broken up and sent to the blast furnaces.

The remaining 85 tons of concentrate is sent directly to the blast furnaces and smelted raw. Thus 62 per cent. of the concentrate is nodulized, 14 per cent. sintered, and 24 per cent. reduced direct.

The two blast furnaces are 25 and 30 feet long respectively, 4 feet wide, and 9 feet deep. They are fed with a charge consisting of varying proportions of nodulized, sintered, and raw concentrate, together with converter slag. The proportion of coke to concentrate averages about 15 per cent. The matte produced contains 45 per cent. Cu, and is treated in converters of the Pierce-Smith basic-lined type.

The Refining of Copper.—The crude copper, whether obtained from the blast furnace, the reverberatory furnace, or the converter, contains, in greater or less proportions, sulphur, the metals which may have been present in the ore, and sometimes, but rarely, selenium and tellurium. The most common impurities are iron, lead, arsenic, and antimony, those occasionally present being zinc, nickel, and cobalt. Silver is always present, and generally gold, both metals often occurring in quantities that can be profitably extracted.

The process of refining is conducted both by dry and by wet methods. In the former cases the operations are carried on in reverberatory furnaces, and in the latter by electrolysis. When the copper contains gold and silver in sufficient amounts, and when there is a demand for specially pure metal for electrical work, electrolytic refining is always adopted. In modern practice this method is widely employed, but for the production of commercial "tough" copper, and of the copper castings which have to be manufactured into tubes, sheets, fire-box plates, and the like, refining in the reverberatory furnace is still extensively carried on; it is also necessary in a modified form for the production of the anodes required in the electrolytic processes.

The process of refining in reverberatory furnaces is conducted with one or other of the following objects :—

(*a*) The removal of the impurities from copper with the subsequent casting of the metal into forms suitable for the manufacture of sheets, tubes, plates, etc., and into ingots for the manufacture of alloys.

(*b*) The purifying and partial toughening of converter copper, and the casting of the resulting metal into anodes for electrolytic refining.

The operations of the process and the size and construction of the furnaces for these two objects present considerable differences. Those having the first object in view will now be considered.

Copper Refining with the Production of Castings for Rolling into Plates and Sheets, drawing into Tubes and Wires, etc.—The furnaces usually employed in England are of moderate dimensions only, as with such furnaces less difficulty is experienced in keeping the copper at a "pitch" suitable for castings which have to be subjected to very severe mechanical treatment. The typical refining furnace, which takes a charge of 20 to 25 tons, is shown in Figs. 52 *a*, *b*, and *c*. The chief dimensions are—Hearth, 18 feet long by 12 feet wide ; fire-box, 6 feet 6 inches by 4 feet 6 inches, having a depth from the top of the fire-bridge to the fire-bars of 4 feet 6 inches. The fire-box is lined with 9 inches of best silica bricks and 9 inches of a commoner kind.

The sides of the furnace are of 9-inch or 12-inch best hard burnt silica bricks laid as headers, with a backing of commoner bricks. At some works the sides consist of 9-inch silica bricks with an inner lining of 9 inches of ganister tamped in around a template. The roof is of 12-inch silica bricks. There is an opening for the admission of air in the middle of the roof about 6 inches within the fire-bridge, and two smaller openings nearer the sides.

In the back wall of the fire-box there is also an opening through which the fire-bridge can be fettled.

The bottom or hearth is of ganister or siliceous sand which should not contain less than 95 per cent. of silica, and is put in in two layers of 10 inches each, as described (p. 84). At some refineries the hearth consists of two courses of 12-inch silica bricks set on end. It is generally built, whatever its structure, on a platform of brickwork below which are three parallel vaults, which run from the front of the furnace to the ashpit. The fire-bridge is strengthened by a cast-iron conker-plate.

Between the conker-plate and the adjacent wall of the fire-box is a space of about 6 inches, through which air is circulated to cool the fire-bridge. The furnace is charged through the side door. The copper is laded and the slag skimmed through the door in front. Poling and rabbling by hand are also done through this door. The entire furnace is encased in cast-iron plates, and is firmly braced together by buckstays and tie-rods. The buckstays are best of 8 or 10-inch I beams set together in pairs.

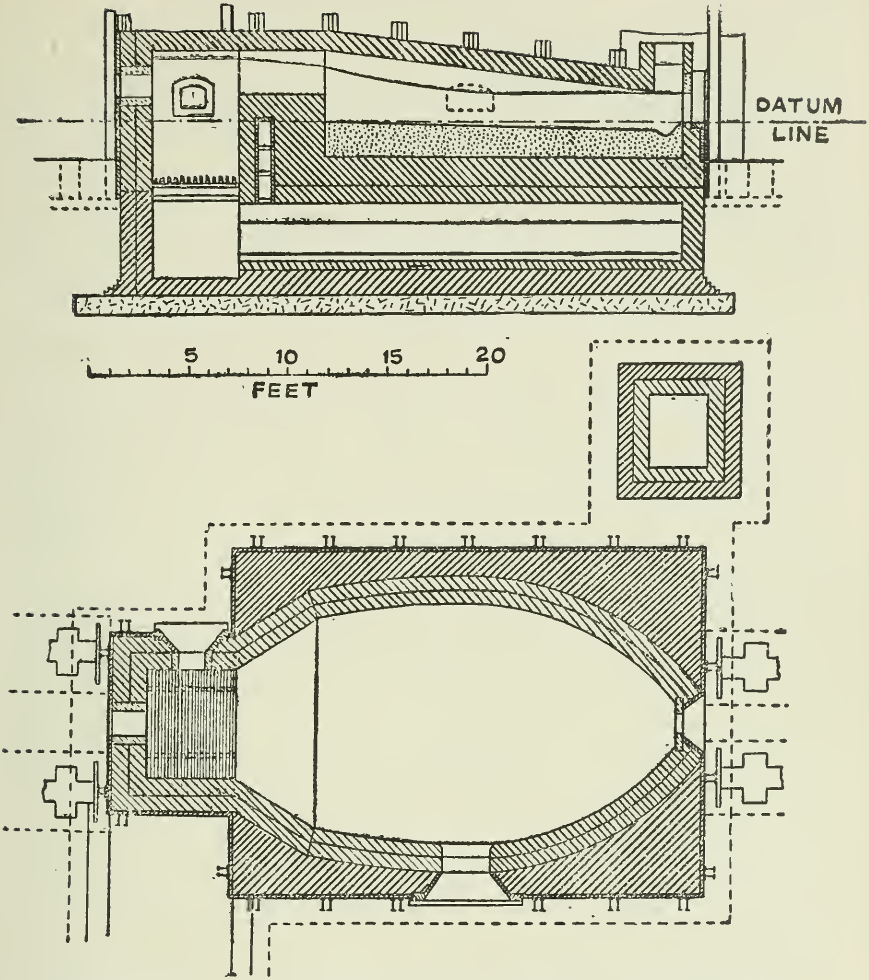
The coal used should be free-burning and give a long flame. It should contain but little sulphur, as copper when refined readily absorbs SO_2. The ash, too, should not be high, and not fusible, or the clinkers will give much trouble.

In most works the furnace gases pass by a downtake to a large underground flue common to several furnaces, and thence to a tall chimney stack, but at the refinery of the Rio Tinto Company at Port Talbot each furnace, with hearth 18 feet × 13 feet, has a chimney stack about 70 feet high.

The Refining Process.—The objects are to remove the sulphur, and as much as possible of the arsenic, antimony, and other impurities which are present in the crude copper, in order that it may be suitable for the manufacture of alloys ; also and especially, to give it the physical properties of toughness, malleability, and ductility which are essential to its application in engineering and other industries ; and to cast it in the forms required for these uses.

The furnace, having its sides and the fire-bridge fettled—that is, repaired with ganister after the working of a previous charge—is charged with pigs of crude or blister copper through the side door.

The pigs are piled up as high as possible, especially near the fire-bridge, until they completely fill up the furnace from the bed to the roof. When the charging is completed, the fire is made up, and the metal rapidly heated until it begins to melt and the upper pigs are just trickling. The port holes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Figs. 52*a* and *b*.—Copper Refining Furnace—Vertical and horizontal sections.

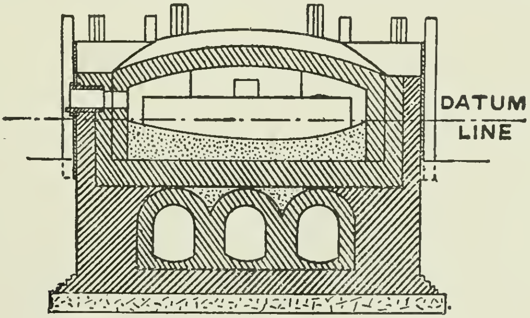

Fig. 52*c*.—Copper Refining Furnace—Transverse section

in the roof are then opened, and air allowed to enter freely, at the same time the temperature is maintained, so that the charge melts slowly down and is well oxidized.

As soon as the charge is thoroughly melted, it is skimmed and kept molten with free exposure to air. During this stage the metal will " work "—that is, it will be in a state of apparent ebullition, due to the escape of SO_2, which will be given off over its entire surface, a frizzling sound being emitted. When it has ceased working it is again skimmed, and is then sometimes " poled " for a short time with a thick green pole to shake out SO_2. The copper will now usually not be sufficiently oxidized, it is, therefore, rabbled until it contains about 6 per cent. of Cu_2O. The rabbling may be effected in two ways, by " flapping," or by a blast of air.

Flapping is the older way, but is still largely practised. It consists in striking the surface of the metal very forcibly with an iron rabble in such a manner that it is violently splashed about.

Air-blast rabbling, which is always employed when the charges are large, as in the refining of converter copper for casting anodes, is accomplished by inserting iron pipes, generally two, through the roof near the fire-bridge, and two through openings in the furnace sides, and forcing compressed air through them either on to the surface of the copper or below it. Rabbling by means of compressed air is also practised in many ordinary refineries. It has many advantages, as it not only shortens the time of oxidation, but enables the hard manual labour of flapping to be dispensed with. The oxidation of the copper by either method requires a longer or shorter time, generally one to two or three hours, according to the amount of oxidation which has been effected during the melting of the charge, and of the impurities present.

The metal is skimmed from time to time during the rabbling stage, and after each of the later skimmings is tested in order to ascertain if the sulphur has been expelled and the metal is sufficiently " dry "—*i.e.*, more or less saturated with Cu_2O.

The testing consists in taking out a small quantity known as the " seal," " proof," or " button sample " in a small iron ladle, and observing whether its upper surface rises or sinks during solidification. If it rises, the copper still contains sulphur, and must be further oxidized. If the copper has not " risen," about 14 lbs. are taken out in a large ladle and allowed to solidify. If the metal rises, the rabbling is resumed, and continued until a ladleful taken out, not only ceases to rise on solidification, but sets with a distinct depression on its upper surface. This is called a " set," and the metal " set-copper."

The copper will now contain about 6 per cent. of Cu_2O, and is in an exceedingly brittle condition. A small quantity is taken out in the test ladle and broken in a vice, when the appearance of its upper surface and its fracture will indicate the extent to which it has been oxidized. If satisfactory, the metal, after being first skimmed clean, is " timbered " in order to remove the greater part of the Cu_2O. This is carried out as follows :—

Anthracite in coarse powder or charcoal is charged through the front door in sufficient quantity, and immediately ten or more logs of green wood about 8 inches diameter and 3 or 4 feet long are thrown in. The front door is closed by a fire-tile and luted, and the fireplace is filled up with coal.

In about 30 or 40 minutes the door is taken down and the copper tested for toughness.

If the refiner has been right in his estimate of the number of logs required, the copper will be generally nearly tough. A few more logs are then thrown in, and the thick end of a long pole of greenwood (hard wood is best, such as beech, oak, or elm) plunged into the melted copper, and kept there by a forked iron upright placed below its outer end.

A test sample is now taken out in the small ladle, broken in a vice, and its fracture examined. If it shows a depressed surface, and its fracture a brick-red colour, the copper is " dry," and requires more poling. If the surface is flat and the fracture salmon-coloured and of fine silky appearance, the copper is at " tough pitch."

An ingot is now cast, and one end forged hot to a thin edge, cooled in water, and the edge then turned over and hammered flat. No traces of cracks or brittleness should be shown. If these tests are satisfactory, the pole is taken out, the coal and charcoal pushed back a little from the door, and the metal laded out in iron ladles, which have been dipped in thin clay luting, into copper or iron moulds. The ordinary ladles hold about 25 lbs. of copper, but at the refinery of the Rio Tinto Company at Port Talbot, " bull-ladles," which hold from 200 to 600 lbs., are in use, and very much shorten the operation of casting. These ladles are suspended from overhead travellers, running on girders which carry them to the moulds, and are furnished with long handles, so that they can be easily filled and emptied.

The moulds for ingots and small slabs are pivoted so that they can be tipped and the castings dropped into water boshes.

The former are always of copper. In casting cakes of large and moderate sizes, the moulds have iron sides, but a cake of copper for their bottoms, in order to ensure soundness. If the copper becomes dry during lading, another log of timber is put in, and also the pole. If it becomes overpoled, the coal and charcoal are partly skimmed off, and the copper allowed to oxidize a little. During the lading, proofs or button-samples to determine the pitch must be taken very often, and certainly before each casting intended for the manufacture of tubes and the like.

When arsenic and antimony are present in the crude copper, caustic soda and lime are repeatedly added towards the end of the rabbling stage, until the yellow metal test shows that they have been almost completely removed. The test is carried out as follows :—

The copper is alloyed with zinc in the proportions of 60 to 40, and the alloy is cast in an iron mould in the form of a square cake, about 4 inches by 4 inches, and about 1 inch in thickness. The cake is allowed to cool, nicked, and broken under a steam hammer. As long as over certain very small amounts of arsenic and antimony are present the fracture will be either crystalline, or will at least show bright streaks running more or less from the top to the bottom of the cakes.

The products of the refining process are tough refined copper and refinery slag. The composition of refined copper is given on p. 57.

The refinery slag contains from 20 to 50 per cent. of copper as silicate, Cu_2O, and as shots of the metal. It also contains the impurities which were present in the crude copper with the exception of those that have been volatilized. It goes back to one of the previous operations for the extraction of its copper.

When the copper is intended for casting heavy cakes for the manufacture of locomotive fire-box plates, which have to contain from about 0·3 to 0·6 per cent. of arsenic, it is first refined as described above, and the arsenic is then added in the desired proportions either as metallic arsenic, or as white arsenic (As_4O_6) mixed with charcoal.

The Reactions and Changes which occur in the Process.—The first stage of the process is one of oxidation, in which the impurities, most of which have a stronger affinity than copper for oxygen, are oxidized together with much of the copper. Some of the Cu_2O formed dissolves in the copper, and exerts a powerful oxidizing influence on them.

The sulphur is oxidized, and passes off as gaseous SO_2. The arsenic is oxidized to As_4O_6 and As_2O_5, but the oxidation is never quite complete, and traces of the metal will remain in the refined copper.

The As_4O_6 is volatilized and the As_2O_5 will enter the slag. Antimony is similarly oxidized, part to Sb_4O_6, which is volatilized, part to Sb_2O_5, which goes into the slag, while part remains in the copper as metal. Arsenic and antimony are never completely removed in the refining process, and traces or more always remain in the refined copper. Bismuth is only very partially oxidized. Iron is oxidized and passes into the slag. Tellurium and selenium are but partially oxidized.

The second stage is one of reduction. Its object is to reduce the Cu_2O contained in the copper to the metallic state. But as pointed out already on p. 58, the whole of the oxide must not be reduced, but a certain amount must be left in the copper, or the metal will be brittle or wanting in toughness. The manner in which this Cu_2O acts has not been definitely ascertained. It is believed, however, that the oxides of the foreign metals which are present in the copper are without injurious effects so long as they remain as oxides, and are only harmful when reduced to the metallic state; also that the presence of a certain amount of Cu_2O tends to preserve them in the oxidized condition (see p. 58).

The action of the timbering and poling is especially efficacious in reducing the Cu_2O, as the gases and water vapour evolved by the action of the molten copper on the green wood cause the metal to be violently thrown about, so that every part of it is brought into contact with the coal or charcoal floating on its surface.

The timbering has also another effect; it removes mechanically the SO_2 which the copper may contain at that stage of the process.

Best Selected Copper.—The process by which this copper was made was devised in Swansea, about the beginning of the eighteenth century, for the purpose of obtaining pure copper from Cornish ores containing tin. It is now rarely, if ever, employed for this purpose, and is chiefly interesting in its application to the extraction of gold from white metal.

The term " best selected " is still, however, often applied to refined copper of special purity. The process essentially consists in the partial reduction of the copper in white metal. The white metal is charged into a roaster furnace and slowly melted down, with the admission of air in such a manner and amount that only a portion of the Cu_2S is oxidized into Cu_2O.

This Cu_2O acts on part of the Cu_2S, forming metallic copper.

The entire charge, which now consists of unoxidized Cu_2S and some metallic copper, is skimmed and tapped out into a row of sand or iron moulds at the side of the furnace. The first five or six moulds will be found to contain a lower layer of metallic copper, and an upper one of white metal, termed *regule*, which is easily detached.

The pigs of copper are termed " bottoms," and if the operation has been properly carried out they will contain all the gold which was present in the white metal, but only part of the silver, so that the process cannot be used for separating the whole of the latter metal. They will also contain nearly all the tin and much of the arsenic and antimony.

They are remelted and cast either into anodes for the electrolytic separation of the gold and silver, or in some works into hollow shot for the manufacture of copper sulphate, when the precious metals become separated in the form of mud, and can be recovered.

The *regule* is charged into another roaster furnace and roasted to blister copper. When this copper is refined it will contain only very small amounts of impurities. It is termed " best selected copper."

The "Direct" Process of Copper Refining.—This process was devised and introduced by Messrs. Nicholls & James, at the works of the Cape Copper Company, Briton Ferry, near Swansea, S. Wales, in 1891.

The ordinary operation of roasting white metal to blister copper is omitted, the process being carried on as follows:—White metal containing about 75 per cent. of copper is roasted in a Prosser gas-fired furnace with mechanical rabbles—a modification of the Brown straight-line furnace—until only about 3 or 4 per cent. of sulphur is left in it. This is charged into a refining furnace together with such a proportion of raw unroasted white metal that when the whole is melted copper and sulphur dioxide will result in accordance with the reaction:—

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

The exact proportions of raw and roasted white metal have to be determined by experiment for each charge by melting together small quantities of each in a Cornish crucible. The entire charge will weigh about 15 tons. On melting, the charge boils vigorously, copious volumes of SO_2 being given off in accordance with the above equation. When the whole of the copper has been reduced, it is skimmed free from slag, rabbled to a " set," then toughened and cast into ingots in the ordinary way.

The slag contains copper, and some is added to the next charge, the remainder going to the white metal furnace.

Partial Refining for the Production of Anodes.—Copper, when cast direct from the converter, gives anodes which are rough on the surfaces and more or less vesicular in structure, hence, and also from the impurities they contain, they are irregularly acted on in the electrolytic vats, and, by the breaking off of pieces, lower the grade of the auriferous and argentiferous mud. They also contaminate the solutions in the vats. To avoid these disadvantages, the copper is subjected to a partial refining and toughening before being cast.

As very large quantities of metal have to be dealt with, and especially because the refining operation need only be carried far enough to produce anodes with a smooth surface and of moderate malleability, containing about 99·3 per cent. of copper, furnaces of large capacity and with deep hearths are employed.

At Anaconda the largest furnace has a hearth 28 feet by 14 feet, and a capacity of 110 tons. The bottom is constructed of four courses of silica brick, the three lower being each of 12 inches, and the working bed of 20-inch bricks, all set on end.

At the plant of the United States Smelting Company, at Chrome, New Jersey, a maximum charge of 186 tons was cast from one furnace into anodes of 500 lbs. each in five hours and fifteen minutes, using a Walker's casting machine, and the average weight of six consecutive charges was 138 tons.*

Very large furnaces, up to 400 tons capacity, are used for anode casting. These are fired by oil or powdered coal, and green poles of wood are used to reduce the oxygen content.

At the works of the Michigan Smelting Company, Houghton, Michigan, where the copper is very free from impurities (having been obtained from native copper), and requires but little refining, a furnace with a hearth 23 feet by 14 feet, and a fire-box having a grate of 5 feet by 6 feet, has treated and cast a charge of 177 tons in twenty-four hours, the ordinary charge varying from 90 to 145 tons, according to the supply of copper available. The copper is cast into ingots, plates, and wire bars, by a Walker casting machine using copper moulds.†

For the remelting of cathodes, the refining furnace at Chrome, New Jersey, may be cited. As this copper is only liable to contain sulphur from the copper sulphate solution, which may have lodged in cavities in the cathodes, the treatment is a simple oxidizing fusion with subsequent toughening. The furnace employed has a hearth 34 feet 3 inches by 14 feet 5 inches. The walls are lined with magnesite bricks to a little above the metal line, where there is a course of chrome brick and above it silica brick.

The cathodes are charged into the furnace through three doors by means of a charging machine, closely resembling the charger, suspended from an overhead girder traveller, which is used in charging open-hearth steel furnaces, but with this difference, that the load of cathodes (about 2,000 lbs.) is carried on a peel, from which it is simply pushed off. The metal is cast into wire bars. About 180 tons of cathodes can be treated in one charge.

The Process of Refining Converter Copper.—The operations at Anaconda, which fairly represent the practice followed in all the chief refineries, are as follows:—

The metal from the converters is brought in ladles and poured into the refining furnace through the side door in quantities of about 5 tons at a time, any scrap which is available being charged in first. Until the furnace is about half full it acts simply as a reservoir. Oxidation by compressed air, blown through iron pipes which just dip below the surface of the metal, is now begun. During the blowing additional ladles of metal are brought from the converters and poured in until the furnace is full. The blowing is continued until the metal becomes "set copper." The slag is now skimmed off and poling of the metal begins. Long poles, 6 to 8 inches thick at the butt ends are now put in, three or four at a time, through the front door, their ends being plunged well below the surface of the copper and held down.

As they burn away they are pushed further in. At the beginning of the poling their action to a certain extent is mechanical, the metal is agitated and the SO_2 dissolved in the molten copper shaken out; after a short time charcoal or anthracite is thrown in, and the reduction of the Cu_2O commences. The poling is continued only until the samples which are laded out and cast into small ingots solidify with an even flat surface. The mechanical tests which are necessary for tough pitch copper are not required, as the anodes have only to be sound, clean, and even castings, with but moderate toughness.

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* *Eng. and Min. Journ.*, July, 1907.

† *Mineral Industry*, 1907, p. 370.

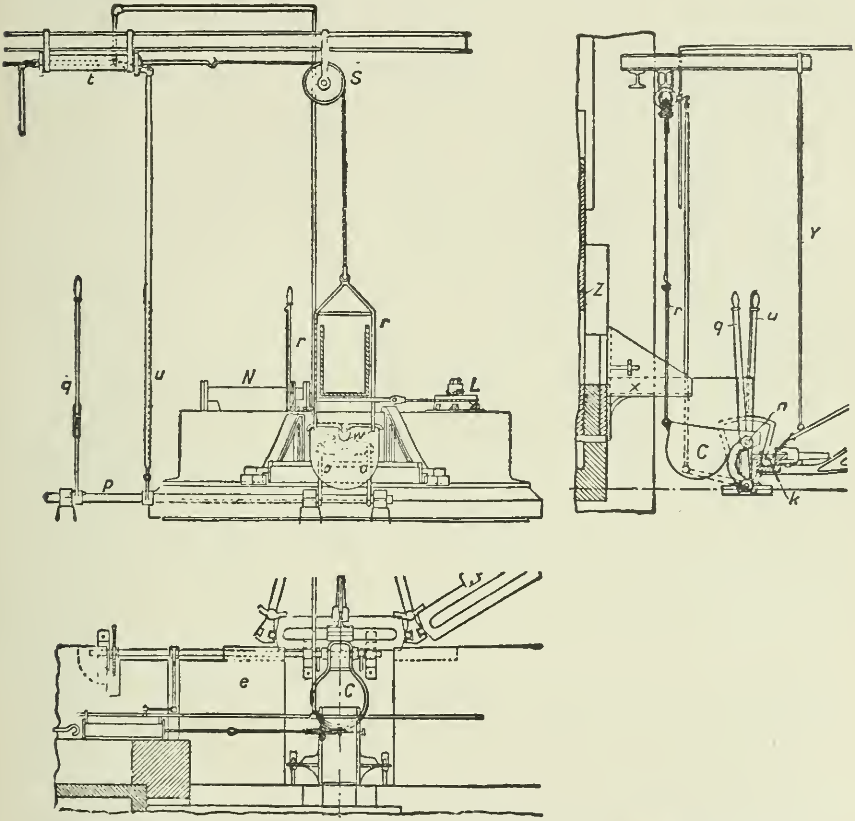

Fig. 53.—Tilting and Pouring Mechanism for Ladle of Refining and Casting Furnace.*

When these large charges are worked, the use of hand- or even of bull-ladles is totally inadequate, casting machines of several types have, therefore, been introduced, and are everywhere employed.

At Anaconda the copper is tapped through a long narrow vertical slit, which is rammed with a mixture of loam and anthracite, so that it can be cut away gradually and the metal allowed to flow out gently. The metal flows along a spout into a ladle of about 800 lbs. capacity, Fig. 53.

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* Levy, *op. cit.*, p. 225.

The ladle is suspended in such a manner that it can not only be tilted for pouring, but can be moved towards and from the moulds as required.

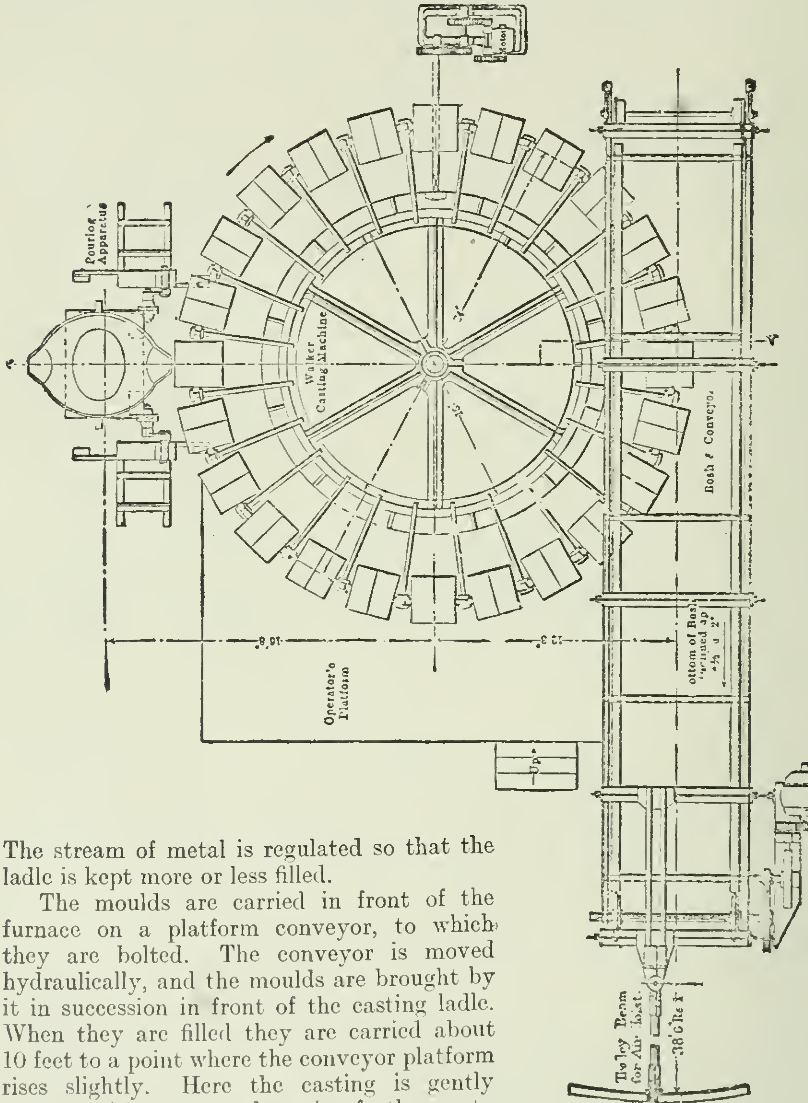
Motor
Pouring Apparatus
Walker Casting Machine
Bosh & Conveyor
Operator's Platform
Up
Trolley Beam for Air Hoist
38'6"

Fig. 54.—Walker's Casting Machine for Converter Copper.*

The stream of metal is regulated so that the ladle is kept more or less filled.

The moulds are carried in front of the furnace on a platform conveyor, to which they are bolted. The conveyor is moved hydraulically, and the moulds are brought by it in succession in front of the casting ladle. When they are filled they are carried about 10 feet to a point where the conveyor platform rises slightly. Here the casting is gently sprayed with water, and passing further on to the end wheel of the conveyor, where the mould is inverted, the casting falls into a tank of water in which is another conveyor, which carries it to the store or yard.

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* *Eng. and Min. Journ.*, May, 1908.

At many works the Walker casting machine (Fig. 54) is employed not only for anodes, but for wire-bars, cakes, etc. The machine consists of a circular horizontal wheel, which carries a series of moulds. It is revolved by a motor, so that each mould is brought in succession in front of the casting ladle to be filled. The moulds are arranged so that they can be tilted when the metal has solidified, and the casting be dropped into a water bosh, where it is received by a conveyor and transported to the store.

Refining in Tilting Furnaces.*—At El Paso a pair of 145-ton tilting furnaces are used for partially refining the blister copper and casting it into anodes. They resemble, in some respects, a tilting open-hearth steel furnace. The hearth is lined with magnesia brick. The hearth frame is of steel, resting on wheels adapted to the curved bearing bars, and is tilted for skimming and casting in the same manner as the steel furnaces. The furnaces are oil-fired. The copper is poured into a tipping ladle, and thence into the moulds on a revolving casting machine.

The Extraction of Copper by Wet Methods.—The wet processes for the extraction of copper from its ores have not, as a rule, been profitable ; a notable exception, however, is the method of treatment carried on at Rio Tinto in Spain (p. 161), where exceptional conditions prevail. The extraction of copper from low-grade ores by wet processes has, however, received special attention during recent years, and many of the most important American copper-producing companies are working on this problem, while at several plants operations are being carried on on a very large scale, notably at Chuquicamata, Mexico. This has been due to a certain extent to the development of extensive deposits of oxidized ores poor in copper and not amenable either to ordinary concentration, or flotation, or to smelting ; but treatment by leaching has not been confined to these, but has extended to ores in which copper exists wholly or partially as sulphides.

For low-grade ores or tailings in which the copper exists as sulphide, flotation, with subsequent roasting of the concentrate and smelting in reverberatory furnaces, is in most cases more profitable than leaching. Such has indeed been the case at Anaconda, where the proposed extensive scheme of leaching all the sandy tailing has been modified, flotation having been now adopted for current tailing, and leaching only for the old accumulated tailing. Leaching, however, still holds the field for poor oxidized ores, although attempts are being made to apply flotation to them also by first converting them partially or wholly into sulphides, but this conversion is still in the experimental stage.

The successful leaching of copper ores depends upon the nature of the ore and local conditions, so that, until those have been thoroughly studied, it is impossible to say which method of treatment would be the most economical. In this connection the most important points to be considered are—the nature of the ore, the cost of sulphuric acid, and the cost of power. Except upon a large scale the treatment of ore by wet processes is not generally profitable.

The work accomplished in actual practice so far indicates that the leaching solution will, as a rule, be a dilute solution of sulphuric acid, and as an abundant supply of cheap acid is imperative, it will be necessary in many localities to utilize the fume from smelting operations, notably the gases from roasting furnaces, for its production.

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* Courtenay de Kalb, *Mining and Scientific Press*, May, 1918.

Ores in which the copper exists as sulphides require to be first roasted, as these minerals are not soluble in dilute sulphuric acid, and are only partially attacked by other ordinary solvents.

At Rio Tinto (Spain), however, where unique conditions prevail, the massive cupriferous pyrites has for many years been treated without previous roasting (p. 161).

"The direct electrolytic solution of copper from raw or roasted ore has been tried, but has proved a failure, if for no other reason than the imperfect electric contact shortly after the process has been started."*

The chief disadvantages and difficulties attending leaching processes may be summarized as follows:—When fine crushing is necessary for an oxidized ore, and the raw ore is treated direct, the presence of slime interferes with the percolation of the solvent solutions and the wash water, but this can be greatly diminished or prevented by roasting. Of course, the effect of roasting in such cases is merely to improve the physical condition of the material.

All the solvents in use attack other constituents of the ore as well as the cupriferous minerals, thus giving rise to foul solutions and causing useless consumption of the solvents themselves.

Very large vats are required if the operations are conducted on an extensive scale, as dilute solutions only can be employed.

Leakage from the vats and spilling from the launders with consequent loss of copper are difficult to prevent completely.

The cost of pumpings and transferring the liquors during the various stages of the operations.

Losses of copper in the tailing and wash water.

If electrolytic precipitation is employed for the separation of the copper, a large consumption of energy is necessary for the precipitation of the metal owing to the high resistance of the dilute solutions. When the solutions also contain a considerable amount of impurities, there is a further waste of energy.

When the ores are suitable for treatment and the condition as to locality, amount, and low cost of mining are favourable, they can be leached with profit, even if they contain only from 0·5 to 1·5 per cent. of copper.

Nature of the Ores, etc., which are suitable for Treatment.—The so-called oxidized ores, which contain copper wholly as oxide, carbonate or sulphate, and in which calcium or magnesium carbonate and ferrous or manganese oxides are present in only small amounts. Silicate of copper, however, is not acted on by the ordinary solvents.

Cupriferous pyrites which have been burnt in the manufacture of sulphuric acid, known as "burnt ore."

Low-grade ores containing copper as sulphides require a preliminary roast, but pyritic ores generally with 2 or more per cent. of copper can, as a rule, be best treated by pyritic smelting. Spanish pyrites containing about 3 per cent. of copper are, however, satisfactorily treated at Rio Tinto by a special leaching process (p. 161).

Oxidized ores from which the cupriferous sulphide minerals have been separated by wet concentration.

Poor tailings as at Anaconda (p. 155).

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* Hofman, *Metallurgy of Copper*, p. 404.

Copper mattes will also yield their copper to leaching processes after they have been roasted, but this procedure is rarely if ever practised now, as dry methods are infinitely more suitable.

The Solvents.—A perfect solvent should possess the following properties, but it is needless to say all are more or less imperfect :—

It should dissolve as completely as possible the copper and metals which it is desired to extract in whatever state of combination they exist in the ore. It should attack in the least degree possible the other constituents.

It must not be expensive, and a large proportion of it should be recoverable.

The solutions obtained should permit of the precipitation or recovery of the metal by economical processes in a useable or marketable form. Unfortunately, no solvent possesses these properties in their entirety.

The chief solvents are the following :—

Water.—The old workings of mines, also tailing dumps that have been long exposed to the oxidizing action of the air, frequently furnish water containing sufficient copper sulphate to make the recovery of the copper remunerative. At the Copper Queen, Arizona, water is, in fact, run into some of the old workings to dissolve the copper sulphate, and is afterwards pumped out and the copper precipitated by iron. Water is also the main solvent in the Mackay process.

Sulphuric Acid, H_2SO_4.—Sulphuric acid is the solvent which is in most general and extensive use. The carbonates of copper and the black oxide (melaconite) are readily soluble in dilute sulphuric acid, but the red oxide (cuprite) is decomposed into CuO and Cu, and must first be oxidized by roasting or weathering before the ore is leached. Further, the dilute solutions of the acid which are employed have no action on silver, so that when this is present in an ore and has to be extracted, common salt must be used in conjunction with them as at Anaconda (p. 156).

Hydrochloric Acid.—See the Henderson process, in which hydrochloric acid is used in conjunction with common salt (p. 158). It is a more powerful solvent than sulphuric acid, but its transportation presents great difficulties, and it can only be made use of in or near alkali works, where it is produced as a by-product.

The following solvents are of secondary importance, and the results obtained by them in actual practice have so far generally been disappointing.

Sulphurous Acid, H_2SO_3.—The action on copper carbonates and oxides is similar to that of sulphuric acid. It is the solvent employed in the Neill process (p. 165).

Ferric Sulphate, $Fe_2(SO_4)_3$.—The old Siemens-Halske process was based on the use of this salt as a solvent. It had been given up, but its successful application to ores containing chalcocite and chrysocolla has been described by Van Arsdale.* Treatment and washing occupy 12 days. The solution is then electrolysed and ferric sulphate regenerated. The average extraction was 78 per cent.

Ferrous Chloride, $FeCl_2$.—This reagent forms the basis of the Hunt and Douglas process (p. 160).

Ammonia, NH_3.—A solution of ammonia to which some salt of ammonia has been added seems to be suitable as a solvent with an ore having a calcareous gangue that is readily attacked by acids.* Considerable difficulties have been encountered in its application, owing to losses due to volatilization and absorption, but these appear to have been minimized or overcome in the scheme now in operation at the Calumet and Hecla Mine, Michigan (p. 163).

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* *Trans. Amer. Inst. Min. and Met. Eng.*, Feb. 1926.

Precipitants.—The precipitation of the copper from the solutions obtained by leaching is effected chiefly by iron, but during recent years electrolysis has been adopted at some plants, notably at Chuquicamata.

Iron.—The cheapest scrap iron procurable, or pig iron at Rio Tinto, is in general use. But as in some localities a sufficient supply at a reasonable cost is difficult or often impossible to obtain, it has been proposed to use spongy iron produced by reducing the iron oxide in crushed roasted pyrites with coal, or producer gas, in reverberatory furnaces. Spongy iron is an ideal precipitant on account of the large surface it affords and its rapid action. For its preparation Croasdale advocates the use of a muffle furnace which can be made air-tight,† and as the spongy iron whilst red hot is immediately oxidized by air it must be cooled in air-tight hoppers, or be discharged from the furnace with water. In the latter case it must be kept under water until ready for use. The following reactions occur when copper is precipitated from sulphate or chloride solutions :—

$$CuSO_4 + Fe = Cu + FeSO_4$$
$$Cu_2Cl_2 + Fe = 2Cu + FeCl_2$$

According to the first equation, 0·88 lb. of iron will precipitate 1 lb. of copper, whilst 0·44 lb. is required in the latter, but " in actual practice about 2 lbs., more or less, are consumed per pound with a cupric salt owing to the formation of basic ferric salts and the liberation of free acid or ferric salt." ‡

There are other precipitants, such as H_2S, SO_2 under pressure, CaS_5, and Na_2S, but they are of little importance, rarely employed, and only under special circumstances.

Electrolysis.—Electrolytic precipitation of the copper from the solution obtained by leaching with sulphuric acid is held to be the best method for the purpose by several distinguished metallurgists, whilst others equally distinguished give the preference to iron. It must be remembered, however, that there may be cases in which either method may be more suitable than the other.

Electrolytic precipitation is carried on in vats furnished with insoluble anodes, and aluminium plates or starting sheets of copper as cathodes. Copper is deposited on the cathodes, and the sulphuric acid set free at the anodes gradually accumulates in the electrolyte. The current is passed in until the electrolyte is poor in copper, which is then returned to the leaching department for the treatment of fresh ore.

The special advantages of electrolytic precipitation are the regeneration of the sulphuric acid when this acid is the solvent, and the production of the copper in a purer form than when the common precipitant iron is employed

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* Hofman, *Metallurgy of Copper*, p. 404.

† *Eng. and Min. Journ.*, Feb. 1915, p. 328.

‡ Hofman, *Metallurgy of Copper*, p. 404.

Among the chief disadvantages of the process are the cost of the plant and the expense of generating the electricity, of which there is a large consumption, due to the low percentage of copper in the solutions which have to be treated.

The method has also inherent defects. If much iron is present, $Fe_2(SO_4)_3$ forms in the electrolyte and gives rise to a loss of energy, as being a solvent of copper it attacks the metal on the cathode taking it into the solution again. The introduction of sulphur dioxide to convert the ferric into the ferrous salt has been successfully used. The process as developed by W. E. Greenawalt * consists in leaching oxidized or roasted sulphide ores with sulphuric acid, reducing the ferric salts in solution with sulphur dioxide, electrolytically depositing the copper, agitating the spent electrolyte with copper sulphide precipitated from part of the weak liquors, electrolysing and using the electrolyte for leaching a fresh charge.

The introduction of insoluble anodes of fused magnetite has removed the disadvantages attending the lead or antimonial lead hitherto in use, although the latter were fairly satisfactory if the leaching solutions were not contaminated with chlorides. These anodes are rectangular in section, hollow, and are electroplated with copper in the interior.

Outline of Wet Methods and Plant.—The extraction of copper by wet processes as usually practised consists in leaching the ore, raw or after roasting, and of the proper degree of fineness, with a suitable solvent in vats fitted with false bottoms, and precipitating the copper from the resulting solutions with iron, or by other means.

The vats in which the ore is leached are generally constructed of wood, tarred, or in some plants lined with lead ; they are also built of reinforced concrete coated with asphalt, and of acid-proof bricks.

Simple percolation of the solvent and wash water is usual, but agitation in Dorr classifiers and in Brown (Pachuca) vats has been introduced, the former at the Butte and Duluth Mine, Montana, and the latter at the plant of the Minerals Recovery Company, of Los Angeles, California.

Only the rich solutions are sent to the precipitation plant, the weak solutions after the addition of fresh acid being used for leaching fresh ore.

The precipitation of the copper by iron is effected by causing the cupriferous solutions to pass through a series of wooden vats, usually lead-lined, furnished with false bottoms of strong lattice work to carry the scrap iron. In some cases the solution is allowed to flow through long troughs containing scrap or pig iron similarly supported.

The precipitated copper is known in commerce as " copper precipitate " or " cement copper," and is always more or less contaminated with impurities. Electrolytic precipitation is also practised, and yields a purer metal.

Examples of Practice—*Chuquicamata* (Chile).—The mine is situated at Chuquicamata in Northern Chile, and according to Mr. Pope Yeatman, as regards tonnage and contents of valuable metal, is the greatest known copper deposit in the world. The reserves of oxidized ore in April, 1915, amounted to over 300,000,000 tons containing 1·5 to 2·0 per cent. of copper. The deposit consists chiefly of brochantite ($CuSO_4$, $3Cu(OH)_2$), copper oxysulphate, together with some chalcanthite ($CuSO_4$, $5H_2O$), and atacamite ($CuCl_2 + 3Cu(OH)_2$), while sulphides make their appearance in the deepest parts explored.

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* *Trans. Amer. Inst. Min. and Met. Eng.*, Jan. 1924.

A typical analysis of the oxidized ore is as follows :—*

Moisture,	0·30	per cent.
SiO_2,	67·48	,,
CaO,	0·61	,,
CuO,	2·66	,,
Cl,	0·40	,,
HNO_3,	0·05	,,
SO_3,	1·76	,,
S (as sulphide),	0·03	,,
Al_2O_3,	13·39	,,
Fe_2O_3,	1·86	,,
MgO,	0·24	,,
MnO_2,	0·02	,,
Na_2O,	3·46	,,
K_2O,	0·84	,,
Loss on ignition,	6·80	,,
Total,	99·90	,,

The ore near the surface is higher in chlorine and nitrates.

The plant was estimated to produce 150,000 tons of copper in 1927. The process entails crushing the ore to about ½-inch mesh, leaching with sulphuric acid, eliminating the greater part of the chlorine by treatment in agitators with metallic copper, precipitating the remaining copper from solution by electrolysis, and melting the cathodes into commercial bars. The treatment of the cuprous chloride formed in the dechloridizing agitators, for the recovery of the copper, is either by smelting, or by dissolving the cuprous chloride with salt and electrolizing, or by treatment with metallic iron to form cement copper.

What makes the process chosen particularly applicable for the Chuquicamata ores is that the ore itself carries more than enough sulphuric acid for the solution of the copper, and that, on precipitation of the copper from this solution, acid sufficient for the solution of the next batch and an excess besides is regenerated, which will allow the discarding of solutions if necessary to avoid fouling of them by continual use.

A further and important advantage is that brochantite, although insoluble in water, is readily soluble in a cold dilute solution of sulphuric acid.

The following description of the plant and method of working is abstracted from an important paper by C. A. Rose, presented at the Second Pan-American Scientific Congress, Washington.†

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* Pope Yeatman, *Eng. and Min. Journ.*, Feb. 1916.

† *Eng. and Min. Journ.*, Feb. 1916; see later description, ***Eng. and Min. Journ.***, 1927, vol. cxxiv., pp. 49 and 445.

The leaching plant consists of leaching vats, each 150 feet long by 110 feet wide by 16 feet deep, set end to end, and solution tanks, which are placed at a somewhat higher elevation. The leaching vats are spanned by two travelling bridges, one for charging the ore and the other for discharging the leached residue. The residue is removed by a 5-ton clam-shell bucket, which discharges on to a belt conveyor.

The vats and tanks are built of re-inforced concrete lined with a 1 to 1¼-inch layer of asphalt mastic. The mastic consists of 1 part of refined Trinidad asphalt and 4 parts of sand. The leaching vats have a false bottom constructed of 6-inch by 6-inch timbers laid 10 inches apart, with 2-inch by 6-inch planks 3 inches apart placed crosswise over them. On this is special cocoa-matting, and on the top of the cocoa-matting is another layer of 2-inch by 6-inch planks ½ inch apart. When the vat is first charged a 1-foot layer of coarse material is spread over this false bottom, thus forming a sand filter. Each vat has eight 6-inch openings spaced evenly over the bottom for removing the solution. All piping is of lead-lined iron, and the pumps are made of type-metal. The first leaching solution is introduced by upward percolation, and is allowed to remain in contact with the ore from 36 to 48 hours; the succeeding solutions are run in on the top of the ore. The solution contains cupric chloride in addition to copper sulphate, and as this would interfere with the precipitation of copper in the electrolytic plant, it is, therefore, removed by converting it into insoluble cuprous chloride in a dechloridizing plant.

The dechloridizing plant consists of concrete pneumatic agitators of the Parral type ; in these the liquor is agitated with cement copper.

The solution flows by gravity from the leaching vats to the dechloridizing plant. In passing through the mills the chlorine is precipitated as cuprous chloride. The precipitate is held in suspension and carried along by the liquor through the mills and into Dorr-thickening tanks, where the cuprous chloride pulp is separated from the clear solution. The pulp is delivered from the Dorr thickeners to an Oliver filter. The filter cake from this machine is mixed with limestone and coke and smelted in a blast furnace; black copper and calcium chloride slag are produced. The treatment of the cuprous chloride precipitate has been tried also by electrolysis and cementation, and the results obtained indicate that the cementation method will be the most suitable. The cuprous chloride will be dissolved in brine and passed over scrap iron, when the copper will be precipitated.

The clear solution from the Dorr thickeners is pumped to an asphalt-lined cement tank holding 1,815 cubic metres, from which it flows by gravity to the electrolytic vat house.

The electrolytic vat house was equipped with 1,098 electrolytic vats in 1927, each 19 feet by 3 feet 6 inches by 4 feet 10 inches deep (inside dimensions), all constructed of re-inforced concrete lined with asphalt mastic. The anodes were of " Chilex," a special alloy made in an electric furnace at the plant, and consisting of copper and silicon with small amounts of lead, tin and manganese.

Anaconda.—As the result of a long series of experiments on a large scale at Anaconda, it was intended to treat the whole of the sandy tailing by roasting and leaching, and the construction of a plant having a capacity of

2,000 tons per day was commenced. In the meantime the success of the flotation process for the treatment of copper tailings had been established, and it was then decided to adopt the process for current tailing, and leaching only for the old tailing which had accumulated to the amount of 20,000,000 tons, and in which some of the copper had been oxidized by weathering.

The following account of the plant erected and the process followed for the treatment of 2,000 tons of old tailing per day is abstracted from two valuable papers by E. P. Mathewson[*] and L. S. Austin[†] respectively:—

The process in brief is to subject tailing that has accumulated for years, and that contains 0·50 to 0·65 per cent. of copper and about 0·687 oz. of silver per ton, to a brief roasting at a temperature calculated to convert the copper sulphides into sulphate and oxides. The resultant roasted product is leached with dilute sulphuric acid together with some common salt, the copper-bearing acid filtrate being sent to launders, there to be precipitated on scrap iron. The precipitate containing from 50 to 70 per cent. of copper is transferred for treatment to the anode furnace of the converter department.

The excavated tailing is sent by cars and belts to the roasting department. In this department there are 28 roasters of a modified MacDougall type in four rows; they are 20 feet in diameter, and have air-cooled shafts and arms. Each furnace has six hearths with fire-boxes on opposite sides of the third arch. The hearths are maintained at a low red heat. The common salt is not added to the furnace charge, but in leaching vats. Beneath each furnace there is a revolving iron cylinder lined with small pipes, through which water circulates, by which the roasted material is cooled. Each pair of coolers discharges into another cylinder, in which the cooled product is mixed with about 1 per cent. of water for the purpose of dust prevention, and then sent by belts to the leaching department.

In the leaching building are ten large leaching vats of redwood, 50 feet diameter by 14 feet deep, in two rows, each of 1,100 tons capacity. These vats have a grated slat-bottom covered with cocoa-matting, the matting being held down and protected by wooden gratings having openings 4 inches square. These openings become filled with roasted tailing, which prevents the matting from being worn by the water used for sluicing. In the bottom of each vat are seven 10-inch sluicing gates. The building for the storage of the solutions adjoins the leaching building, but is 17 feet lower, so that the vats can drain into the solution tanks, of which there are five, each 50 feet diameter by 14 feet deep.

In these tanks the solutions used for leaching are stored, and are pumped to the top of the leaching vats by means of hard-lead centrifugal pumps. The floors of both buildings are of concrete, coated with an asphalt-tar mixture. These floors slope towards a gutter, which leads to a sump. Each leaching vat, after it has been filled with the roasted tailing, receives a charge of 15 tons of common salt, which is spread over the surface of the ore; this is to dissolve the silver which it contains. The roasted tailing is then leached with successive charges of dilute sulphuric acid containing 8 per cent. of NaCl, and with weak copper liquors from the vats strengthened with fresh acid, finally followed with wash water. The leaching is done by continued downward percolation.

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[*] *Eng. and Min. Journ.*, April, 1915.

[†] *Eng. and Min. Journ.*, April, 1916.

The precipitation of the copper and silver is accomplished with scrap iron. The precipitation plant consists of three concrete launders of an available section of 4 feet by 8 feet above a false bottom. Each launder is 190 feet long, and is divided into three equal compartments. Any one of these compartments can be cut out for cleaning without interfering with the flow of solution through the others. The precipitate is washed off by a hose jet from the scrap iron surfaces, and, going to the bottom of the launder, is flushed into a settling tank parallel with and adjoining the launders. The presence of NaCl in the solution is said to prevent the copper from plating on the iron, a soft spongy precipitate of cement copper being formed which can be easily sluiced off with a hose. After washing and draining it is excavated by a clam-shell grab, loaded upon cars, and taken to the anode furnace.

*The New Cornelian Copper Company, Ajo, Arizona.**—According to the report of the general manager, the ore body was estimated to contain 12 million tons of low-grade carbonate ore, containing about 1½ to 2 per cent. Cu. An analysis by Wedge of the crushed ore in the vat charges is as follows :—

SiO_2,	67·21
Fe,	4·88
Al_2O_3,	12·60
CaO,	0·21
MgO,	1·66
MnO,	0·19
S,	0·08
Cu,	1·55

The ore is ground to ¼-inch mesh.

The operation of leaching is conducted in two parallel blocks of six vats each ; they are constructed of massive reinforced concrete with walls 8 inches thick, strengthened by concrete buttresses. Each vat is 88 feet square by 18 feet deep, and holds a charge averaging 5,000 tons of crushed ore. The bottom of the vat slopes gently towards the solution launder, which is like an elongated well extending the full width, and is 4 feet by 5 feet in vertical section. Each vat is lined with 6-lb. lead, protected against wear by a lining of 2-inch boards. The bottom of the vat is protected by a false bottom of 2-inch Oregon pine planks, laid close together and supported by 4-inch by 12-inch beams 16 inches apart. The planks are perforated by ⅜-inch holes. The solution is forced by lead-lined centrifugal pumps from the well through the perforations ascending through a 15-foot column of ore and discharging at the ends of the vat into launders placed between successive vats, whence it is delivered by other pumps to the next vat, and so on through the series.

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* Courtenay de Kalb, *Mining and Scientific Press*, Feb. 9th, 1918.

The charging is done by a special machine, and no spreading by hand is practised. The discharging is effected by an electrically driven clam-shell excavator. Each charge after leaching receives four washes. Every first wash liquor is returned to the regular circulatory system of the plant after having been strengthened with sulphuric acid.

The leaching solution is brought from the electrolytic vats, and will contain on an average 3 per cent. sulphuric acid, 2·5 per cent. Cu, and 2 per cent. Fe as ferric and ferrous sulphates. It is introduced at the last vat, which holds the charge that is receiving its eighth day of treatment, then passes successively through the vats to the one holding the newest charge, from which it issues practically neutral and containing 3 per cent. Cu. It will be seen that only one-sixth of the copper in the solution from the leaching vats is precipitated in the electrolytic vats. In order to avoid too great fouling of the leaching solution a certain quantity is passed to a cementation plant, from which it is run to waste after precipitation of the copper on metallic iron. Before the liquor from the leaching vats is passed to the electrolytic department, it is necessary to reduce the ferric iron to the ferrous state. This is effected by sulphur dioxide in a group of four towers, each 40 feet high by 20 feet diameter, being a specialized type of Glover Tower. The gas enters below and rises against the descending solution. The gas is produced by roasting pyritic ore in Wedge furnaces, and contains about 7 per cent. SO_2 by volume.

In the electrolytic department there are 12 banks of 10 tanks each and 4 banks of 8 tanks each, making a total of 152 tanks. Each tank is 29 feet 7 inches long, 4 feet 9 inches wide, and 4 feet 3 inches deep, all of Oregon pine, lined with 7-lb. sheet lead. Each tank has 84 anodes, 41 inches by 51 inches by $\frac{1}{4}$ inch thick. They are of lead containing 3·5 per cent. antimony. There are 77 cathodes per tank, each 42 inches by 42 inches. Current is supplied by two 15,000 ampère circuits, each carrying 76 tanks in series, equal to a current density of 8 ampères per square foot of cathode surface. The drop of potential between anode and cathode averages close to 2 volts.

The ore body is gradually changing from oxidized into sulphide ores, so that the leaching plant is treating less material and more is going to the concentrators.

The Longmaid-Henderson Process.—This process is used for the treatment of pyrites, containing from about 2 to 6 per cent. of copper, which have been "burnt" in pyrites kilns in the manufacture of sulphuric acid, and is extensively employed in sulphuric acid works working on Spanish pyrites in this country and elsewhere.

The burnt pyrites should not contain more than 6 per cent. of copper. They should contain but little gangue, or an excessive amount of common salt will be required, and there must be at least 1·0 part of sulphur present for each part of copper.

The process in brief consists in the conversion of the copper and the silver and gold, of which small quantities are present, into chlorides, by roasting with common salt; the solution of the chlorides, or any copper which may have escaped chloridization, in water and hydrochloric acid, and the precipitation of the metals by iron. The gold and silver are separated from the copper by electrolytic refining in America, but in this country the Claudet process is generally practised.

The process is carried out as follows:—The burnt ore is ground, at the same time being mixed with from 10 to 20 per cent. of common salt. The mixture, after screening, is charged into reverberatory furnaces, of which there are several forms, the best being those in which the gases from the chloridizing and those from the fuel are kept separate.

In America the Wedge multiple hearth mechanical downdraught muffle furnace is said to have been employed with success. Complete roasting is necessary in order to convert the copper into sulphate, and sodium chloride being present, mutual decomposition results, cupric chloride and sodium sulphate being formed.

The iron should be converted as completely as possible into ferric oxide, so that it may become insoluble. Some chlorine is evolved owing to the action of the SO_3 and O upon NaCl, and at the same time a considerable amount of hydrochloric acid is formed. For a successful chloridizing roast the ground ore and salt must not be coarser than 8-mesh, there must be free access of air and vigorous rabbling, and the amount of sulphur present must be at least equal to that of the copper. Raw pyrites must be mixed with the charge if the ratio of the sulphur to the copper is less than 1 to 1. The gases from the chloridizing furnace, containing SO_2, H_2SO_4, HCl, Cl, and some volatilized Cu_2Cl_2 are led to condensing towers, filled with coke or acid-proof bricks, down which water is allowed to trickle. The liquid from the towers, called tower liquor, is used for leaching the chloridized ore. The leaching of the chloridized ore is carried out in wooden vats, each of which usually contains about 10 tons of ore. The ore is first leached with weak liquor from a previous operation, by which most of the copper is dissolved. This solution is sent to the precipitation vats. The ore is then washed with hot water, producing weak liquor, which is used as the first wash water of another charge. Finally, there are several washings with the tower liquor to dissolve cupric oxide and cuprous chloride, or if this is insufficient with dilute hydrochloric acid bought for the purpose. The residue from the leaching is called "purple ore," and is sold to iron smelters or for fettling puddling furnaces.

The rich copper solution from the leaching vats is precipitated by scrap iron in vats made of wood, tarred and fitted with a false bottom of slats to support the iron. Each vat is filled loosely with scrap iron; the copper liquor is run in and steam turned on until a bright strip of iron held in the liquid no longer indicates the presence of copper in solution. The cement copper is transferred to other vats, in which it is thoroughly washed. It is sold to copper smelters or makers of sulphate of copper, or smelted at the works where it is produced. The cement copper contains nearly the whole of the gold and silver contained in the burnt ore.

By the use of the Claudet process the gold and silver, to the amount of two-thirds of each metal contained in the ore, are separated from the solution from the leaching vats before the precipitation of the copper. This process consists in precipitating the silver from the copper solution by a soluble iodide, silver iodide, which is insoluble in solutions of chlorides, being produced.

The amount of silver in the clear solution is first accurately determined. It is then diluted with 10 per cent. water containing an excess of potassium or zinc iodide over that required for the silver. As some lead is thrown down as PbI_2, the precipitate consists mainly of AgI, PbI_2, and $PbSO_4$. When a sufficient quantity of it has been collected it is well washed with water and treated with metallic zinc and a little hydrochloric acid. Thus the AgI and PbI_2 are decomposed completely, the $PbSO_4$ partly, and a solution containing zinc iodide is obtained which is used over again with the addition of some potassium iodide. The silver is obtained as a metallic sponge mixed with pieces of zinc and containing about 60 per cent. of lead, 6 per cent. of silver, and 0·06 gold, the percentage of the precious metals varying with the amounts present in the ore (Lunge).

The operations including Claudet's process are illustrated by the accompanying diagram (Fig. 55).*

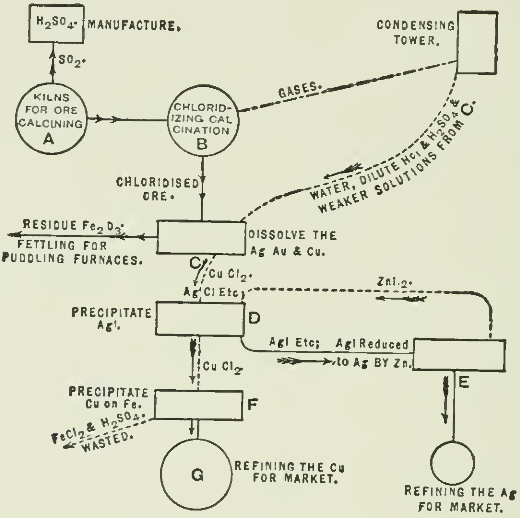
H_2SO_4. MANUFACTURE.
CONDENSING TOWER.
SO_2.
GASES.
KILNS FOR ORE CALCINING
A
CHLORIDIZING CALCINATION
B
WATER, DILUTE HCl & H_2SO_4 & WEAKER SOLUTIONS FROM C.
CHLORIDISED ORE.
RESIDUE Fe_2O_3.
FETTLING FOR PUDDLING FURNACES.
DISSOLVE THE Ag Au & Cu.
C
$CuCl_2$.
AgCl Etc.
ZnI_2.
PRECIPITATE AgI.
D
AgI Etc; AgI Reduced to Ag BY Zn.
$CuCl_2$
E
PRECIPITATE Cu on Fe.
F
$FeCl_2$ & H_2SO_4. WASTED.
G
REFINING THE Cu FOR MARKET.
REFINING THE Ag FOR MARKET.

Fig. 55.—Claudet Process.

A complete description of the process and the plant employed will be found in Lunge's *Sulphuric Acid and Alkali*.

"Several plants for the treatment of burnt pyrites along the lines of the Longmaid-Henderson process with variations are being constructed in the United States, along the Atlantic Seaboard" (Addicks).†

The Modified Hunt and Douglas Process.—This process was used at the Argentine Works of the Kansas City Smelting and Refining Company for the treatment of copper matte. It is conducted as follows:—The matte, after crushing and roasting, is treated with a dilute solution of sulphuric acid. The solution containing copper sulphate and some iron sulphates, is run into a precipitation vat, a solution of ferrous or calcium chloride is added, by which part of the copper sulphate is converted into cupric chloride in accordance with the following equations :—

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* Roberts Austen, *Introduction to Study of Metallurgy*, p. 429.

† *Eng. and Min. Journ.*, Jan. 1917.

$$2CuSO_4 + FeCl_2 = CuSO_4 + CuCl_2 + FeSO_4$$
$$2CuSO_4 + CaCl_2 = CuSO_4 + CuCl_2 + CaSO_4.$$

Sulphur dioxide obtained in roasting the ores is forced into the solution, when cuprous chloride is formed and precipitated, with the simultaneous setting free of sulphuric acid according to the following equation :—

$$CuSO_4 + CuCl_2 + SO_2 + 2H_2O = Cu_2Cl_2 + 2H_2SO_4.$$

The cuprous chloride is collected and treated with either milk of lime or iron, cuprous oxide or metallic copper being produced with the formation of calcium or ferrous chloride.

Milk of lime was used at the Argentine Works, and the cuprous oxide after washing was filter-pressed and smelted in a small blast furnace with charcoal.

The filtrate from the cuprous chloride precipitate, which consists chiefly of sulphuric acid, is freed from sulphur dioxide by blowing hot air into it from an injector, and is used again as a solvent for the treatment of the roasted matte.

The filtrate obtained in treating the cuprous chloride with milk of lime or iron is used again for the chlorination of the copper in the copper sulphate solution from the leaching vats.

The process was abandoned at these works on account of the considerable loss of copper due to the presence of chlorides in the cuprous oxide, even after thorough washing, which caused a large volatilization of copper chloride during the operation of smelting.

Rio Tinto, *Spain*.*—The following account is abstracted from a paper by C. H. Jones, communicated to the American Institute of Mining Engineers in February, 1904. The ore treated is massive iron pyrites containing up to 3 per cent. of copper.

The method adopted is to allow huge heaps of the mineral to oxidize under the influence of moisture and air with subsequent washing out of the copper sulphate by water and precipitation of the copper by iron. The success of the method depends largely upon the state in which the copper exists in the ore. When the copper occurs as chalcopyrite, $CuFeS_2$, it will not oxidize by simple exposure to the air. If it is in the form of covellite, CuS, the oxidation proceeds very slowly. The best form for solution is copper glance, Cu_2S, which constitutes the bulk of the copper in the Rio Tinto ore. When the ore is freely exposed to air and moisture, some ferrous sulphate is formed in accordance with the reaction—

$$(1) \quad FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4.$$

This ferrous sulphate becomes readily oxidized by the air to ferric sulphate :

$$(2) \quad 2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O,$$

and it is due to the action of this ferric sulphate on the copper sulphides that the copper is rendered soluble, thus—

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* *Cf.* J. Irving, *Eng. and Min. Journ. Press*, 1921, vol. cxiii., p. 714.

$$(3) \quad Fe_2(SO_4)_3 + Cu_2S = CuSO_4 + 2FeSO_4 + CuS.$$
$$(4) \quad Fe_2(SO_4)_3 + CuS + 3O + H_2O = CuSO_4 + 2FeSO_4 + H_2SO_4.$$

Reaction No. 3 causes half the copper to go into solution within a few months, while No. 4 requires about two years to extract 80 per cent. of the remaining half of the copper.

The method of working is as follows:—A site is chosen for the formation of the heap, where the ground is impervious to moisture, and slopes so as to enable the copper liquor to collect and run out at the base of the heap. On the ground is first arranged a network of air-flues, 12 inches square, made of rough stones. Vertical chimneys, 50 feet apart, are built in the same manner, while the heap is being made, and connected with the ground flues.

The ore is broken to lumps about 2 to 3 inches across. Lumps and fines are dumped alternately until the height of the pile is about 30 feet, the upper surface being kept level. A heap contains approximately 100,000 tons of ore. The top surface of the heap is formed into squares, by means of ridges, to enable the water to be run locally over the surface of the ore, in order to ensure that all parts are equally washed. During the formation of the heap water is run on to extract the copper sulphate present. The heap is then allowed to oxidize, which it does rapidly, the temperature in the chimneys rising to from 77° C. to 82° C. As the temperature rises the ground flues may be closed, in order to allow the oxidation to spread.

Care must be taken not to allow the heap to take fire. When the oxidation has proceeded as far as is safe, water is run on at the rate of about 50 cubic metres per hour, until the soluble copper salts are extracted. The heap is then allowed to oxidize further, and the washing is repeated. When a year has elapsed the top surface requires "re-tilling," and the squares are arranged where the ridges were before. When the copper is reduced to 0·3 per cent., the heap is considered to be washed, and the material is removed and exported as "washed sulphur ore" for the manufacture of sulphuric acid.

The copper liquor as it runs from the heap contains some ferric iron in solution, which is very objectionable. In order to remove it, the liquor is run over a smaller heap of fresh ore, which reduces the ferric iron—

$$7Fe_2(SO_4)_3 + FeS_2 + 8H_2O = 15FeSO_4 + 8H_2SO_4.$$

This "bed" is laid inside a reservoir formed by a masonry dam across a small ravine, and the liquor, after percolating through the ore, remains in contact with it until required to be drawn off to the precipitating vats.

The principal constituents of the liquor as it enters the precipitation vats are—Cu, 0·4 per cent.; Fe_2O_3, 0·1 per cent.; FeO, 2·0 per cent.; As, 0·03 per cent.; and free sulphuric acid, 1·0 per cent.

The large quantities of FeO and H_2SO_4 are due to the fact that some of the waste liquor from the precipitation vats is used for washing the heaps in addition to fresh water. The copper solution is run from the reservoirs through long trough-like precipitation vats over pig iron, and the copper is precipitated in the form of "cement copper," or "copper precipitate." The vats or troughs are arranged on the slope of a hill, and the liquor passes backward and forward through them until it is discharged from the lowest vat of the series free from copper. The vats are of wood, and range from about 200 to 400 feet in length, and the copper-bearing solution traverses about a mile of vats before the copper is all precipitated. Some of the vats are cut out from the series and cleaned out daily, the pig iron being taken out and the copper removed from it. The dirty-looking precipitate is then removed to the cleaning and concentrating plant.

At the cleaning plant the precipitate, which contains about 70 per cent. of copper, is thrown a little at a time on to a perforated copper plate placed at the head of a long launder, and is washed through the plate by a strong jet of water. The material that does not pass through consists of leaf-copper and small pieces of iron; this is thrown into a heap and sorted to remove the iron. The precipitate that passes into the launder is turned over against the stream of water and by this means concentration is effected.

In the first few yards of the launder is found "No. 1 precipitate," containing Cu 94 per cent. and As not exceeding 0·3 per cent.; following this is "No. 2 precipitate," containing Cu 92 per cent. and As 0·75 per cent.; while lower down is "No. 3 precipitate," containing Cu 50 per cent. and As 5 per cent., as well as the graphite from the pig iron, and the antimony and bismuth precipitated from the liquors. Nos. 1 and 2 are bagged for shipment. No. 3 is made into balls, and sent to the blast furnaces.

The following processes have been or are at present employed on a less extensive scale than the preceding.

The Ammonia Process.—The use of ammonia together with an ammonium salt has been proposed for the treatment of poor oxidized ores or tailing, especially for those containing much calcium or magnesium carbonates, which unfit them for leaching with sulphuric acid.

The process is based on:—

1. Copper oxide will dissolve in ammoniacal solutions, yielding copper-ammonium compounds.
2. Solutions of cupric-ammonium salts are capable of dissolving native or metallic copper, yielding cuprous-ammonium salts.
3. These cuprous-ammonium salts may be oxidized, by air or other suitable oxidizing agents, to cupric-ammonium salts.
4. Copper-ammonium solutions subjected to distillation are decomposed with separation of copper oxide, ammonia being volatilized. The process has been employed at the Calumet and Hecla Mine for the treatment of the old tailing, containing from 6 to 14 lbs. of copper per ton, of which a vast quantity has accumulated. An acid solvent could not be used, as the ore contains too much calcium carbonate. The method introduced at the mine by Mr. Benedict is illustrated in the accompanying diagram (Fig. 56). Leaching is carried out with a solution of cupric-ammonium carbonate, made by oxidising with air part of the leach liquor which contains the corresponding cuprous compound. The liquor contains the equivalent of 30 grams of ammonia per litre before use and the average loss of ammonia is 1·25 lbs. per ton of ore treated.

It has not been practicable hitherto to employ highly dilute solutions, as their solvent capacity is low, and the volume required has been large, necessitating a large and costly installation. In Mr. Benedict's scheme, although dilute solutions are used, a much smaller plant is necessary. The process is described by him as follows.* (For further details, see *Eng. and Min. Journ.*, July, 1917) :—

" The ore is subjected to two leaching operations and two washes, the contents of the four solutions employed being (1) 0·5 per cent. Cu, 1 per cent. NH_3, 0·8 per cent. CO_2 ; (2) 0·35 per cent. Cu, 1 per cent. NH_3, 0·8 per cent. CO_2 ; (3) 0·01 per cent. Cu, 0·08 per cent. NH_3, 0·02 per cent. CO_2 ; and (4) water only, or distillation reject containing only traces of copper and ammoniacal compounds. The first leaching solution contains ammonia, ammonium carbonate, and cupric-ammonium carbonate, and consists of a

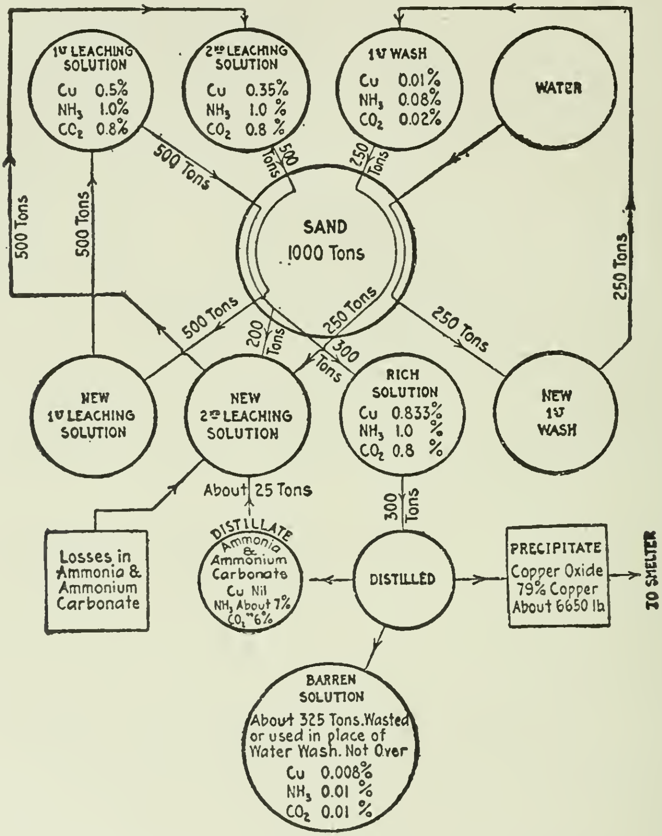
1st LEACHING SOLUTION
Cu 0.5%
NH₃ 1.0%
CO₂ 0.8%
2nd LEACHING SOLUTION
Cu 0.35%
NH₃ 1.0 %
CO₂ 0.8 %
1st WASH
Cu 0.01%
NH₃ 0.08%
CO₂ 0.02%
WATER
500 Tons
500 Tons
500 Tons
500 Tons
250 Tons
250 Tons
SAND
1000 Tons
500 Tons
200 Tons
250 Tons
300 Tons
250 Tons
NEW 1st LEACHING SOLUTION
NEW 2nd LEACHING SOLUTION
RICH SOLUTION
Cu 0.833%
NH₃ 1.0 %
CO₂ 0.8 %
NEW 1st WASH
About 25 Tons
300 Tons
Losses in Ammonia & Ammonium Carbonate
DISTILLATE
Ammonia & Ammonium Carbonate
Cu Nil
NH₃ About 7%
CO₂ " 6%
DISTILLED
PRECIPITATE
Copper Oxide
79% Copper
About 6650 lb
TO SMELTER
BARREN SOLUTION
About 325 Tons. Wasted or used in place of Water Wash. Not Over
Cu 0.008%
NH₃ 0.01 %
CO₂ 0.01 %

Fig. 56.—Flow Sheet of New Calumet and Hecla Treatment.†

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* *Min. Mag.*, 1915, p. 295. (Abstract of paper by C. H. Benedict in *Min. and Scientific Press*, April, 1915.) *Cf.* Benedict and Kenny, *Trans. Amer. Inst. Min. Met. Eng.*, 1924.

† *Eng. and Min. Journ.*, May, 1915.

previous second leaching solution. In conducting the process 1,000 tons of sand (containing about 0·5 per cent. of copper), which is finer than 40-mesh and previously freed from slime, is run into a covered vat, say 54 feet in diameter and 12 feet high. The first solution, amounting to 500 tons, is fed from above, and the flow from the bottom regulated to obtain the desired period of contact of the solution and ore. The first portion of the effluent solution, say 200 tons, is poor in copper and low in ammonia, and is run into the sump for the second leaching solution. Afterwards the effluent, a further 300 tons, is richer in copper, and is sent to the distilling plant. On distilling, copper oxide is precipitated, and ammonia and ammonium carbonate are formed. The two latter are used in forming the second leaching solution, and the solution remaining after distillation containing traces of copper, ammonia, and ammonium carbonate, may be employed as the second wash. After the right amount of first solution, 500 tons has been delivered to the leaching vat, 500 tons of the second solution is run in at the top, and subsequently the first and second washes of 250 tons each follow. The second leaching solution after passing through the vat becomes the first leaching solution for the next batch of sand. The first wash after passing through the vat goes to the sump for the second leaching solution. The second wash becomes the first wash for the next batch of sand. The total amount of solution is about 1,500 tons for each 1,000 tons of tailing, and of this amount only 300 tons goes to the distilling plant. The relative amount of each solution is so regulated that their composition shall practically remain constant. It will be seen that as only one-fifth of the usual circulating solution goes to the distilling plant, the cost of erecting the whole installation is substantially lowered."

The Neill Process (SO_2 as solvent).—In this process sulphur dioxide, generated by "burning" pyrites in kilns (pyrites burners), is employed as the solvent. The native oxides and carbonates of copper are readily dissolved by solutions of SO_2, so that ores containing these minerals or sulphide ores which have been roasted, calcium and magnesium carbonates being present in only small proportions, are suitable for treatment.

The ore, after grinding, is charged into wooden revolving barrels with water, and SO_2 is passed in through one of the trunnions. When the copper has been dissolved the solution of $CuSO_3$ is run into vats, steam is blown in until the boiling point is reached, the SO_2 is expelled, and the copper is thrown down as a heavy dark red crystalline precipitate of cupro-cupric sulphite ($CuSO_3$, $Cu_2SO_3 + 2H_2O$), some $CuSO_4$ being formed. About 55 to 75 per cent. of the copper is thus precipitated, and the remainder is obtained by passing the solution over scrap iron. The cupro-cupric sulphite, after being washed and dried, is reduced to metallic copper in a reverberatory furnace.

The greater part of the copper is precipitated without the use of scrap iron, and this is an advantage in remote districts, where that precipitant is dear or difficult to obtain.

According to Hofman,* the process at Caconino, Arizona, was not successful for mechanical reasons, but tests at the works of the Montana Ore Purchasing Company, Butte, with ore roasted in MacDougall furnaces, gave a total yield of 90 per cent. of copper with a direct extraction of 64 per cent. as $CuSO_3$, Cu_2SO_3.

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* Hofman, *op. cit.*, p. 418.

Butte-Duluth Mine, Montana.—The extensive deposit of oxidized ore overlying the sulphide ores, which has been neglected for many years, is now being treated by the following wet process.* The copper minerals present are said to be the green and blue carbonates together with the silicate, but no analysis is given. The ore was at first crushed to ½ inch and leached in vats with a 10 per cent. solution of sulphuric acid, but the percentage of copper obtained only ranged from 50 to 70 per cent., and finer crushing prevented percolation. It was hence decided to leach the ore in modified Dorr classifiers. The Dorr plant first erected consisted of five classifiers made of wood, each 4 feet 6 inches wide and 15 feet long, placed in series. The first three were used for contact with acid, and the last two for washing. It was found that this arrangement did not allow the ore to remain in contact with the acid a sufficient length of time to secure a high rate of extraction.

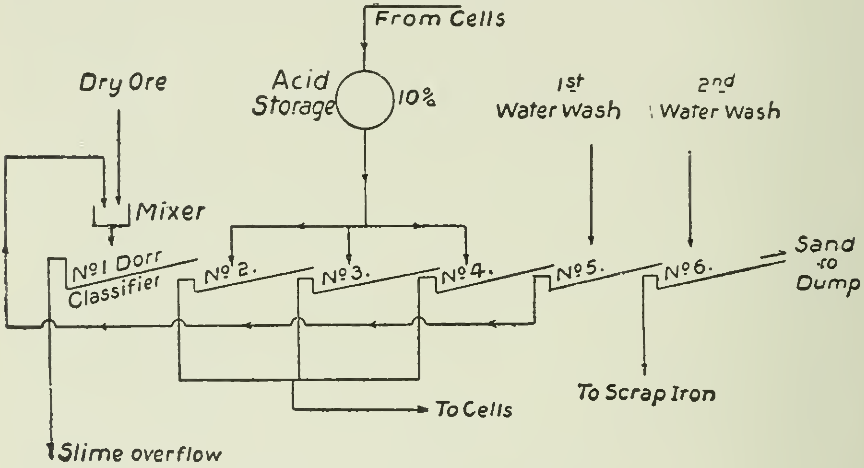

Fig 57.—Butte-Duluth Flow Sheet.

Consequently arrangements were made to place two additional classifiers, each 30 feet long, at the head of the former series, making seven in all, with a total length of 135 feet, and to lengthen the 15-feet machines to 30 feet, in order to permit the ore to remain in contact with the acid a still greater length of time.

A further change is being effected. A new set of machines is being installed, 8 feet wide, placed in series as before. The first four for acid treatment, 30 feet long, are followed by two for wash water, each 15 feet long. At four strokes per minute this should give more than 60 minutes' contact of ore and acid, and ensure a high rate of extraction.

Each machine is set with an overlap of 3 feet and a slope of ⅞ inch per foot.

The method of operation is shown in the flow sheet (Fig. 57).

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* Hertzig, *Trans. of Inst. of Min. and Met.*, 1914, vol. xxiii., p 451.

The slime overflow at present goes to the old leaching tanks; later this will probably be superseded by some mechanical system of agitation. The copper is precipitated from this solution on scrap iron.

The ore is fed to the first classifier and a dilute solution of sulphuric acid added. The slime discharges over the bottom end, and is collected in one of the old leaching vats in the bottom of which a bed of crushed ore is placed to act as a filter. The coarse pulp passes over the head and drops into the second classifier. Fresh solution of 10 per cent. (66° Beaume) acid is added to No. 2 classifier, and also to Nos. 3 and 4. The two succeeding machines are used for wash water. The wash water from No. 5 machine is conducted back to be used for mixing with the dry ore and fed on to No. 1 machine, while that from No. 6 is passed over scrap iron to precipitate the copper.

The solution as it comes from the classifiers contains about 6 per cent. of acid and 4 to 5 per cent. of copper, and is led to an electrolytic plant.

The solution from the electrolytic cells contains about 8 per cent. of acid and about 1½ to 2 per cent. of copper. This is brought up to a standard of 10 per cent. of acid and pumped back to be used for leaching.

Precipitation of Copper from Mine Waters.—Copper in solution as sulphate occurs in the water from mines in many localities, also in the water draining from old tailing dumps and old mine workings which have been long exposed to atmospheric oxidation.

Noteworthy examples of the extraction of the copper from mine water are afforded by the practice at Butte, Montana, and at the Copper Queen Mines, Arizona.

Precipitation at Butte.—The procedure followed at the High Ore Plant, Butte, as described by Mr. J. Febles,* is briefly as follows:—The amount of water flowing averages 1,200 gallons per minute. The average copper content is 0·05 per cent., and the extraction is 98·6 per cent. The temperature of the water issuing from the mine is 85° F., and after passing through the precipitation plant 54° F. On leaving the mine, the water passes through the first set of flumes, three in number, parallel to each other, each 4 feet wide, 2 feet deep, and 300 feet long, with a fall of 2 per cent. These flumes are filled with scrap iron, such as rails, pipes, rods, and bars. The iron is continually turned over in order to dislodge the precipitate. Every few days one of the flumes is cut out of circuit, so that the iron may be temporarily removed and the precipitate washed into the settling tanks at the end of the flumes. The water afterwards passes down a second series of flumes, 8 feet wide, with an incline of 2½ per cent., and length of 500 feet. Along these flumes there are settling tanks spaced 75 feet apart. The settling tanks are large wooden boxes, of the same width as the flumes, about 15 feet long and 8 feet deep, and so arranged that the precipitate can be sluiced through a hole in the bottom into drying vats. After passing through the flumes, the water is pumped by bronze centrifugal pumps to the top of a tower, consisting of a heavy wooden frame filled with scrap iron too big for use in the flumes. This tower is 130 feet long, 8 feet wide, and 19 feet high, with a settling tank extending the whole distance beneath it, and provided with baffle boards at the sides to prevent the escape of splashing water. The water is then sent to another tower, and afterwards to two parallel flumes, 9 feet wide by 300 feet long, filled with tin cans and small scrap. Thence it goes to a series of five towers, and after passing settlers runs to waste. The figures given by Mr. Febles show that 95 per cent. of the copper content is recovered in the flumes before going to the first tower, so that the towers, subsequent flumes, and second set of towers yield very little. The precipitate after being air-dried contains approximately 70 per cent. Cu.

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* Abstract in *Min. Mag.*, Sept. 1913, of Mr. Febles' paper, *Trans. A.I.M.E.*, vol. xlvi., p. 177.

*Precipitation at the Copper Queen Mine.**—At the precipitation plant of the Copper Queen Consolidated Mining Company, Lowell, Arizona, the mine water, which is pumped from the shaft, flows through a flume 3,600 feet long and enters a series of six large vats containing heavy scrap iron, thence it passes into eight sets of flumes containing lighter scrap. The barren water flows into a set of five settling tanks, a portion of this water is then pumped back to the mines, and the remainder is run to waste. The six vats are of red wood, 20 feet in diameter, 10 feet deep, with a heavy false bottom grating, to support the scrap iron. Each vat is provided with two doors near the bottom, through which the cement copper can be flushed into launders leading to the settling tanks. The vats are connected with the flumes in such a way that the water may be cut off from any vat, while the cement copper is being flushed out. From the vats the water passes to the series of eight double parallel flumes with small connecting launders at the end of each flume. Each double flume is 200 feet long, 4 feet wide, 45 inches deep, has a uniform slope of 1 per cent., and is supported upon strong trestle work. Baffle boards divide each flume into either four or five compartments, and serve to regulate the depth of water. Stoppered holes at the ends of each compartment allow the cement copper to be flushed into collecting launders below. A light railway runs between each double flume, and is used to distribute the iron required for the precipitation. The settling tanks are 10 feet in diameter and 5 feet deep, with a 10-inch by 10-inch circular launder around the periphery. The sludge from the precipitating vats and flumes flows into these settling tanks, the cement copper settles to the bottom, and the clear water passes over the edge into the circular launder, whence it flows into another settling tank, from which a definite portion is pumped back to the mines. The cement copper from the settling tanks is air-dried in shallow wooden boxes, 20 feet long by 15 feet wide and 12 inches deep. The plant is designed to deal with from 300 to 2,500 gallons of mine water per minute, varying according to the seasons. The water as it leaves the mine contains approximately 0·03 per cent. of copper, of which 97·7 per cent. is extracted. About 300,000 gallons are pumped back daily to the upper levels of the Holbrook mine, which were worked out years ago, and the stopes gagged with moderately rich waste. The water percolates through these old workings, leaching out the copper, and is collected in a sump to be pumped back to the precipitating plant.

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* Coats and Allen, *Eng. and Min. Journ.*, Jan. 1915.

ELECTROLYTIC REFINING.

The objects of electrolytic refining are to obtain pure copper suitable for use in the manufacture of wire, conductors for electrical purposes, alloys, and for other industrial applications where a specially pure metal is required, and to recover the gold, silver and valuable metals contained in impure copper.

The importance of the development of electrolytic refining processes for metallic copper is evident from the enormous capacity of the refineries now in operation. The capacity of the United States refineries in 1927 was given by S. Skowrowski,* as 1,444,000 tons per annum.

When two sheets of copper are connected with the terminals of a generator of electricity and placed in a solution of suitable composition, the sheet connected with the positive pole being known as the anode and the other connected with the negative pole being known as the cathode, if a current of suitable voltage and ampèrage is passed, the current will pass from the anode through the solution to the cathode, the impure copper will then be dissolved from the anode and pure copper be deposited on the cathode. The impurities will either dissolve in the electrolyte and foul it or be deposited at the bottom of the tank as " slime."

There are two systems of working the process—the *multiple* or *parallel* system and the *series* system.

In the first the anodes are all connected with one pole of the circuit, and the cathodes with the other, whilst in the second the anode and cathode pairs are connected in electrical series.

In the *multiple* system the anodes are cast plates of crude copper, and the cathodes are specially prepared sheets of pure copper placed between the anode plates.

In the *series* system special cathodes are not required, one side of the anode plate acting as cathode, impure copper, which has been dissolved from the other side of the next plate, being deposited on it as pure copper.

The relative advantages and disadvantages of the two systems are as follows :—

Chief Advantages of the Multiple System as compared with the Series System. —1. Copper of any quality can be treated. Anodes may, in fact, be cast from the converters, but it is better first to partially refine and toughen the copper, as the electrolyte is then not contaminated with impurities for some time, and the efficiency of the plant is increased.

2. Less cost in preparing the anode plates, which are only cast, whilst in the series system they have to be cast and then rolled.

3. A lower voltage is required, and there is less loss through short-circuiting through the mud and sides of the tank.

4. Less cost for labour, as the anodes and cathodes can be placed in and removed from the tanks by mechanical appliances.

5. The vat efficiency with careful work should be 95 per cent. of that which is theoretically possible, against 85 to 90 per cent. in the series system.

6. Less scrap is produced, and the cost of stripping deposited copper from the scrap is not incurred.

7. Less capital is locked up in the electrodes.

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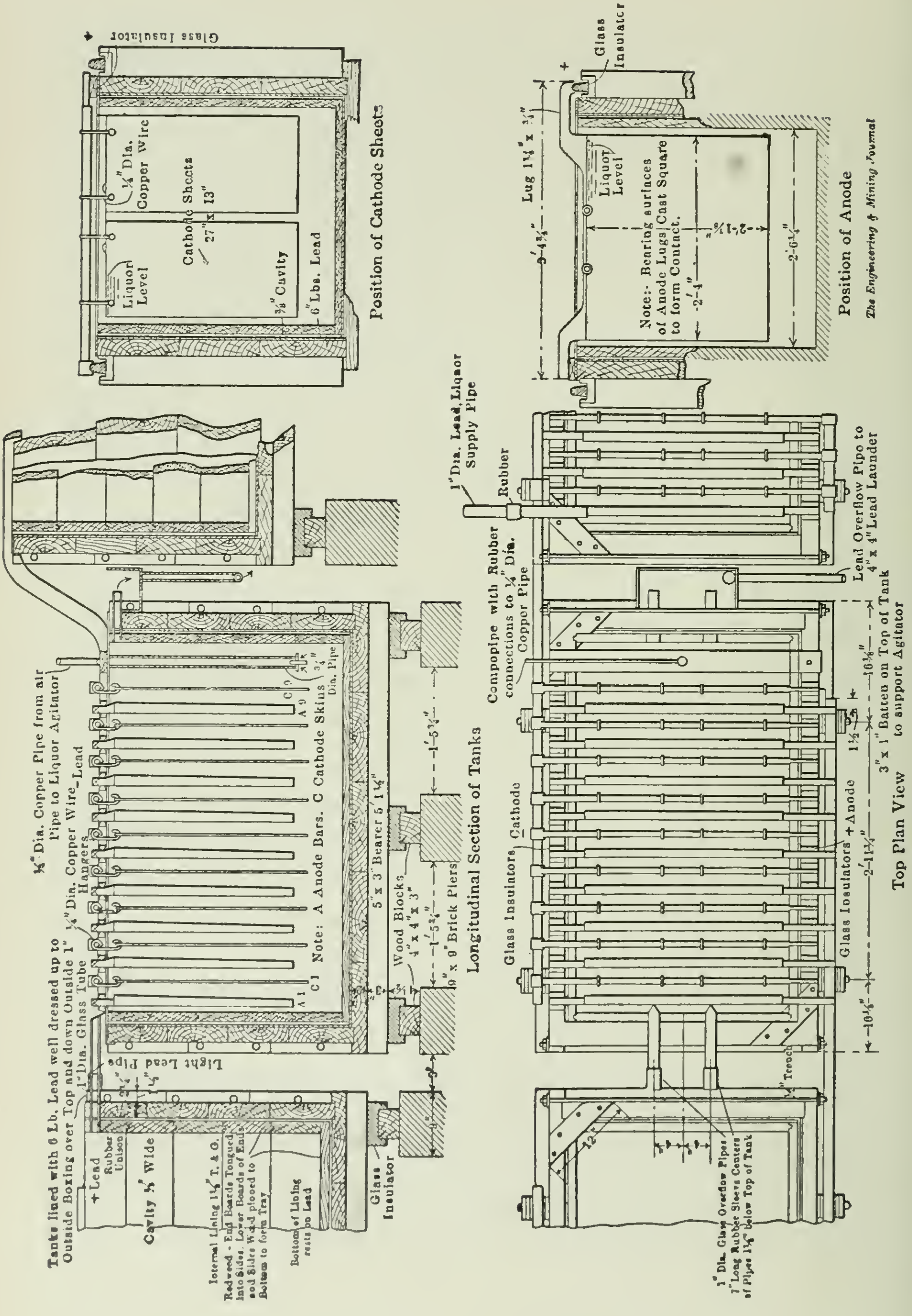
* " Twenty-five Years' Progress in the Electrolytic Refining of Copper," *Trans. Amer. Electrochem. Soc.*, 1927, vol. li., p. 139.


Glass Insulator
+
Glass Insulator
1/4" Dia. Copper Wire
Cathode Sheets 27" x 13"
Liquor Level
3/8" Cavity
6" Lbs. Lead
Position of Cathode Sheets
Lug 1 1/4" x 3/4"
Liquor Level
3'-4 1/2"
Note:- Bearing surfaces of Anode Lugs Cast Square to form Contact.
2'-1 3/8"
2'-4"
2'-6 1/2"
Position of Anode
3/4" Dia. Copper Pipe from air Pipe to Liquor Agitator
1/4" Dia. Copper Wire Lead Hangers
1" Dia. Glass Tube
Tanks lined with 6 Lb. Lead well dressed up to Outside Boxing over Top and down Outside 1"
C A C A
3/4" Dia. Pipe
Note: A Anode Bars. C Cathode Skins
5" x 3" Bearer 5' 1 1/4"
Wood Blocks 4" x 4" x 3"
1'-5 3/4"
1'-5 3/4"
9" x 9" Brick Piers
Longitudinal Section of Tanks
Light Lead Pipe
2 1/4"
1 1/2"
+ Lead
Rubber Unison
Cavity 3/8" Wide
Internal Lining 1 1/4" T. & G. Redwood - End Boards Tongued into Sides. Lower Boards of Ends and Sides Wood pinned to Bottom to form Tray
Bottom of Lining rests on Lead
Glass Insulator
9"
1" Dia. Lead Liquor Supply Pipe
Rubber
Compopipe with Rubber connections to 1/4" Dia. Copper Pipe
Lead Overflow Pipe to 4" x 4" Lead Launder
Glass Insulators
Cathode
Glass Insulators
+ Anode
2'-11 1/4"
10 1/8"
16 3/8"
1 1/2
3" x 1" Batten on Top of Tank to support Agitator
Top Plan View
Trench
12"
1" Dia. Glass Overflow Pipes 7" Long Rubber Sleeve Centers of Pipes 1 1/2" below Top of Tank

The Engineering & Mining Journal

Fig. 58.—Electrolytic Vats, Lithgow. N.S.W.

8. Lower cost of maintenance.
9. Higher silver values may be present in the anodes.

The disadvantages are :—

1. Higher cost of plant.
2. Cost of preparing the pure copper cathode plates which are not required in the series system.
3. The output per vat is less.

The advantages are strongly in favour of the multiple system, and although the series system is employed in a few refineries, the former system is in most extensive use, and is superseding the latter.

The Operations of the Multiple System.—The process consists in the electrolysis of an acidified copper sulphate solution in vats, in which are suspended anode plates of impure copper and cathode strips of pure copper, by which the copper dissolved from the former is deposited as pure copper on the latter. The gold, silver, platinum, and some of the impurities in the anodes settle to the bottom of the vats in the form of mud.

Selenium and tellurium pass into the mud along with the precious metals. Iron, nickel, and zinc form sulphates which dissolve in the electrolyte, but are not precipitated on the cathode. Arsenic, antimony, and bismuth go partly into solution and partly into the precipitated mud. Lead passes chiefly into the mud ; some copper also is always precipitated.

Silver tends to pass over to the cathodes, but in small quantity only, and chiefly when the acidity of the electrolyte diminishes, and to guard against this, a very small quantity of hydrochloric acid is added. Arsenic also, if it has accumulated in the electrolyte, may contaminate the cathode copper, and to prevent this ammonium sulphate has been added, but a frequent removal of the electrolyte is more satisfactory.

The Vats.—These are constructed of Oregon or pitch pine, and are lined with 6-lb. lead. They are generally 10 feet to 15 feet in length and 2 feet 6 inches to 3 feet 6 inches in breadth. The breadth must be sufficient to leave about 3 inches between the side edges of the anodes and the sides of the vat, and the depth to allow 6 inches between the bottom of the anodes and the bottom of the vat. The planks of which the vats are constructed are often first immersed in molten paraffin wax.

The insulation of the vats is important, and is effected at Lithgow (New South Wales) as follows :—Each vat is carried upon two hard wood joists, treated with paraffin, which rest upon glass insulators. These insulators are supported by six square blocks of Oregon pine, which have also been treated with paraffin, and which rest on brick supports.

The vats are arranged in rows of about eight, each vat being 2 inches to 3 inches lower than the preceding one, to assist the circulation of the electrolyte. Circulation in each vat is also promoted by agitation with a small jet of compressed air, care being taken not to disturb the settled mud.

The conductors or " leads " are laid along the long sides of each vat. They are sometimes insulated from the vats by resting in porcelain holders held in brackets on the outside walls of each vat. One of the lugs of each anode rests on one of the conductors, and the other on a glass or porcelain insulator. The cathode sheets are hung from cross bars, which rest at one end on glass or porcelain insulators on the anode lead, and at the other end on the opposite conductor.

The arrangement of the anodes, cathodes, etc., in the vats at Lithgow, New South Wales, is shown in Fig. 58.* One or more electric overhead travelling cranes transport the sets of anodes and cathodes to and from the vats.

The Anodes.—The anodes are of various sizes, ranging from 2 feet 4 inches by 2 feet 2 inches to 3 feet by 3 feet, a common size being 3 feet by 2 feet 6 inches. They are generally 2 inches in thickness, and are cast with lugs for suspension.

In American refineries they are fairly pure, the copper of which they are cast having been partially refined and toughened, to diminish the amounts of impurities, and thus prevent too great a contamination of the electrolyte. They are also thus obtained with flat surfaces, as far as possible, free from irregularities, and the tendency to sprouting common in rough castings is minimized.

Their usual composition is—Cu 98·0 to 99·5 per cent.; Ag traces to 3,000 ozs., and Au 0 to 40 ozs. per ton; As 0 to 2·0 per cent.; small amounts of S, Fe, Bi, Ni, Sb, etc. (*Austin*).

The Cathodes.—The cathode strips are prepared by deposition on rolled copper plates about ⅛ inch thick, cast to a size about 2½ inches longer than the required cathode, and about 1 inch wider. At the Lithgow electrolytic plant the copper plates are first dipped in molten tallow, and after draining off the excess and the tallow has set, each is coated on both sides with a fine coating of graphite. At the edges the sides are coated to a width of about ½ inch by dipping into molten tallow.

After this preparation twenty-four are hung in a vat to twelve anodes, and allowed to remain for two days, when they are withdrawn and a sheet of thinly deposited copper, weighing about 2 to 3 lbs., is stripped off each side. Two slips for suspension are then fitted to each.

At Raritan each electrolytic vat contains twenty-four anodes and twenty-five cathodes, the anodes being spaced 4⅝ inches from centre to centre.

The cathodes are removed every fourteen days, washed, and sent to the refining furnace to be cast into wire bars and ingots.

The Electrolyte.—This is a solution containing 15 to 40 per cent. of copper sulphate crystals, and 5 to 20 per cent. of sulphuric acid.

During working, copper sulphate tends to concentrate in the lower layers of the solution, and the acid in the upper, therefore, in order to maintain the electrolyte uniform in composition it is circulated and also agitated with an air jet. The circulation is effected by allowing the solution to flow from an elevated tank to the first vat, the solution from which flows to the second, and so on until the eighth or the last vat of the series is reached, whence it runs into a sump, and is then elevated and returned to the supply tank.

The solution is heated, by allowing it to flow from the supply tank through a small lead-lined tank in which are leaden coils, through which exhaust steam from the engine is passed. The temperature varies in different works from 40° to 54° C.; but according to Borchers no advantage is obtained by raising the temperature of the electrolyte above 40° C., if the quality of the cathode copper be taken into account.

During the process, the percentage of copper in the electrolyte increases and the percentage of acid decreases; this is remedied by treating the electrolyte in vats fitted with lead anodes, which are insoluble, and the usual copper cathodes, when copper is deposited on the cathodes, and sulphuric acid set free.

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* *Eng. and Min. Journ.*, October, 1910.

The impurities which were present in the anodes gradually contaminate the electrolyte and affect its specific resistance, as shown by S. Skowrowski * and E. A. Reinoso; a portion, therefore, must be periodically removed from the system and replaced by fresh solution. The impure electrolyte is run into lead-lined vats, in which it is boiled with granulated copper, in the presence of air and steam. The solution is then run into crystallizing pans, in which the copper sulphate crystallizes. The copper in the mother liquor is precipitated with iron, or the liquor is evaporated for the recovery of sulphuric acid.

Current Density.—With a high current density the output of electrolytic copper is greater than with a lower, hence it is advisable to use the highest that can be safely applied. In America, it varies between 13 and 30 ampères per square foot. At the Raritan Works, Perth Amboy, N.J., it is 20, and at the works of the American Smelting and Refining Company 15 ampères per square foot. The current density permissible depends, however, on the purity of the anode copper. If this is very impure, and the current density too high, the cathode copper will be contaminated.

Voltage.—This usually ranges from 0·1 to 0·3 volt.

The Anode Mud.—The composition of the anode mud varies with the composition of the anodes; thus the percentage of the Au may range from 0·7 to 2·0, of the Ag 5·0 to 40·0, of the Cu 10·0 to 25·0, of the As and Sb up to 10·0, with more or less Bi, Pb, and Fe.

It is removed from the vats every three months or oftener. The mud is passed through a 40-mesh sieve, to separate any pieces of copper, and is then boiled in a lead-lined vat with sulphuric acid, care being taken to dissolve as little of the silver as possible. By this means the copper is reduced to about 1 per cent., and the iron, bismuth, and most of the arsenic are removed.

The mud is then dried and sent to the gold and silver refinery.

Treatment of Mattes.—The process of Borchers, Franke, and Gunther is carried on at Mansfeld on matte containing 72 per cent. of copper, and is said to be successful, but the operations are beset with many difficulties, owing to the brittleness of the matte, the high voltage, 0·75, required, and the rapid contamination of the electrolyte.

The method of working is similar to the electrolytic refining of metallic copper, but the anodes are of matte.

Electrolytic Refining at the Raritan Copper Works at Perth Amboy, N.J.†—The blister copper is melted in reverberatory furnaces, of which there are six, each of about 225 tons capacity. In this melting but little refining is attempted, although some of the impurities are removed with the slag and the sulphur is practically eliminated. The anodes, which measure 37 inches by 28 inches by $1\frac{5}{8}$ inches, and weigh about 500 lbs., are cast in moulds on a straight-line casting machine. Their average composition is as follows :—

Cu, ...	99·25 per cent.
Ag, ...	70 ozs. per ton,
Au, ...	0·25 oz. per ton,

with from 0·05 to 0·06 per cent. As, Sb, Ni, Pb, Fe, and little more than traces of Bi, S, Se, and Fe.

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* *Trans. Amer. Electrochem. Soc.*, 1927, vol. li. † *Eng. and Min. Journ.*, Oct., 1917.

The anodes are electrolized in tanks in an acid solution of copper sulphate, usually 16 per cent. bluestone with 12 per cent. free sulphuric acid. The voltage is about 0·25 volt per tank.

The multiple system of refining is employed, the anodes and cathodes being connected in multiple and the tanks themselves in series. The electrolytic tanks are of wood 118 inches by 34 inches by 44 inches, and are lead-lined. They are carefully insulated on glass and are so placed that any leakage of electrolyte may easily be detected. There are two tank houses, one of 1,800 and the other of 1,656 tanks. Four circuits of 7,000 ampères in each tank house give a current density of 18 ampères per square foot of cathode surface. The tanks are arranged in nests of 11 cells each, the nests being so placed together so as to circulate the electrolyte in cascade through the tanks. The circulation of the electrolyte is maintained at the rate of 4 gallons of solution per minute per tank. After leaving the lower tank in the cascade the solution drops to hot wells, where it is reheated by means of steam coils to 60° C., and thence pumped to the top of the cascade. Tests have shown that the best conditions for the electrolysis is a circulating solution at 55° C. Each tank contains 28 anodes and 29 cathodes. The cathodes, which are placed between the anodes, are thin starting sheets of copper, 30 inches wide, 37 inches long, and weigh about 8 lbs. each. At the end of ten days the cathodes have increased in weight to an average of 125 lbs. each. They are then taken out of the tanks, carefully washed, and sent to the refining furnace for melting. A second and later a third set of starting sheets follow the same procedure. At this stage the anodes of crude copper have so dissolved that only skeletons of the originals remain.

(The cathode starting sheets are made from blanks of hard-rolled polished electrolytic copper $\frac{1}{3}$ inch thick. These blanks are placed as cathodes in regular electrolytic tanks, and in 24 hours so much copper has deposited on each side of them that it can be easily stripped off in thin sheets, which, after being looped, become starting sheets. To prevent the deposited copper from adhering fast to the blanks, they are covered with a thin film of grease or oil before electrolysis.)

After the third removal of cathodes the solution is siphoned from the tanks. The scrap anodes are sent to the blister furnaces to be re-cast. The slimes are then pumped to a special department, where the gold, silver, and other metals are separated. The total impurities in the electrolyte, such as Ni, As, etc., are kept below 2 per cent. by purifying a certain percentage each day. This is done by a series of crystallizations, whereby the copper in the solution is recovered as " bluestone " and the nickel as sulphate. The acid after the removal of the arsenic is used over again in the electrolyte.

The cathode copper is melted in large reverberatory furnaces of 225 to 250 tons capacity, of which there are six. It is charged into these furnaces with a charging machine, melted, oxidized, poled, and then cast into wire bars, ingots, and other commercial shapes on a circular casting machine. A representative analysis of the refined electrolytic copper would be as follows :—Cu, 99·92 to 99·97 per cent. ; O, 0·02 to 0·07 per cent. ; Ag, 0·001 per cent. ; Au, 0·00001 per cent. ; S, 0·003 per cent. ; Fe, 0·0035 per cent. ; Ni, 0·0015 per cent. ; As, 0·0015 per cent. ; Sb, 0·0015 per cent.

LEAD.

Physical Properties.—Lead is the softest metal in common use, and can be readily scratched by the finger nail. Its softness, however, is diminished when antimony, arsenic, copper, and zinc are present.

A cast ingot of lead, generally called a "pig," yields a very dull sound when struck with a hammer, and the duller the sound the purer the metal. Its approximate purity is also frequently roughly determined by its streak on white paper, and its hardness when scratched with the finger nail.

Malleability and Ductility.—Lead is very malleable, and can be readily rolled into sheets and even into thin foil. On the other hand, its ductility is very low, and it cannot be drawn into fine wire. When the metal is heated to a certain temperature it may be squeezed through an aperture into pipes and solid rods. The operation is termed "squirting," and all lead pipes are thus made.

Tenacity.—The tenacity of lead is lower than that of any other common metal; the tenacity of cast lead being only 0·81 ton (*Rennie*), of sheet 0·86 ton (*Napier*), and of pipe 1·0 ton (*Jardine*) per square inch.

Specific Gravity.—The specific gravity of pure cast lead is 11·35 to 11·37 The specific gravity is diminished by the presence of antimony, arsenic, and copper, or the ordinary impurities found in commercial lead, and is hence a measure of its purity.

Action of Heat.—Lead melts at 327·4° C. When a pig of lead is heated to near its melting point and then broken, the fractured surfaces show a largely columnar structure. The larger the columns the purer the lead. If air be excluded, lead is not sensibly volatilized below a red heat, and it cannot be distilled like zinc; but in the distillation of zinc, or zinc ores containing lead, a considerable amount is carried over by the zinc vapour. With access of air fumes of lead oxide are evolved at a bright red heat, hence the loss of metal, often very great, in smelting operations.

Electrical Conductivity.—Its conductivity for electricity is 10·7, if that of silver be taken as 100.

Atomic Weight.—Its atomic weight is 207·2.

Chemical Properties.—In perfectly dry air lead undergoes no change at ordinary temperatures, but in moist air it becomes dull from oxidation. At its melting point, lead oxide, PbO, is formed, and at a higher temperature oxidation takes place rapidly.

Its best solvent is dilute nitric acid. That of specific gravity, 1·2, is good. Hydrochloric acid has but little action on lead, in compact masses, except when concentrated and boiling.

Sulphuric acid also only acts on it when concentrated (specific gravity 1·76 and over), and boiling. Hence, in evaporating strongly acid solutions in leaden pans, or vessels lined with lead, as, for example, the mother liquors from the crystallization of copper sulphate from the waste acid from refining gold and silver bullion, great care must be taken that the specific gravity should not exceed 1·72.

Lead Oxides.—Lead monoxide, litharge, PbO. The other oxides except red lead, Pb_3O_4, are of little importance in metallurgy, and Pb_3O_4 only in assaying. PbO is produced on a large scale in the cupellation of argentiferous lead. It is a very strong base, and when molten powerfully corrodes clay crucibles, fire-bricks, and furnace materials, forming silicates with the silica they contain. At a dull red heat it is completely and rapidly reduced by carbon, also by carbon monoxide, hydrogen, and cyanogen.

The temperature at which reduction is effected is below that at which CO_2 is converted into CO in the presence of carbonaceous matters, so that CO_2 and not CO is the product evolved—

$$2PbO + C = 2Pb + CO_2.$$

One of its most valuable properties in metallurgy is the power it possesses of forming fusible compounds with various metallic oxides, many of which are infusible alone. Upon this property, together with its power as an oxidizing agent, the following operations depend :—

1. The refining of silver by cupellation.
2. The softening of hard lead.
3. The assaying of alloys and ores of silver by cupellation and scorification.

The amounts of litharge required for the fusion of the principal metallic oxides are as follows :—

1 part of	Cu_2O.	CuO.	ZnO.	Fe_3O_4.	Fe_2O_3.	MnO.	SnO_2.	Sb_4O_6.	Sb_2O_4.	As_4O_6.	As_2O_5.
Requires parts of litharge,	Under 1·5	Under 1·8	8	4	10	10	12	any	5	·4 to ·8	·25 to 1·0

The melting point of litharge is about 883° to 900° C.

The oxidizing action of litharge plays an important part in the treatment and assaying of silver and its ores.

Thus when it is fused with S, Fe, As, Sb, Bi, Sn, Cu, Zn, or Fe, these substances become wholly or partially oxidized, and their oxides either volatilize, or dissolve in the excess of litharge, a corresponding amount of lead being reduced, which combines with any unoxidized part.

Lead Silicates.—When silica is heated with litharge to the temperature at which the latter becomes pasty, a silicate begins to be formed. The fusibility of the silicates varies greatly, the monosilicate, $Pb_2SiO_4[2PbO, SiO_2]$, is as fluid as water, whereas the silicate PbO, $18SiO_2$, is practically infusible. All up to the silicate $Pb_2Si_3O_8[2PbO, 3SiO_2]$ are fusible at low temperatures.

The lead of silicates is not readily liberated by ordinary reducing agents. They are not reduced by carbon, unless some base as FeO and CaO is present which will form a fusible compound with the SiO_2. The lead in all the silicates is completely separated in the metallic state when they are fused with iron. The proportion of iron employed should be at least equal to that required to form a monosilicate, $Fe_2SiO_4[2FeO, SiO_2]$. Similarly, the whole of the lead is separated when they are fused with ferric oxide and carbon in proper proportions, and if lime is present also the reduction of the lead takes place at a lower temperature, and a more fusible slag is produced.

Iron, barium, and calcium sulphides all decompose basic lead silicates at moderate temperatures, thus :—

$$4PbO . SiO_2 + 2FeS = 2FeO . SiO_2 + PbS + 3Pb + SO_2.$$

Lead Sulphate, $PbSO_4$.—This occurs native as anglesite, and is formed when PbS is roasted at a low temperature.

Lead sulphate is not decomposed like other sulphates at a bright red heat, but is wholly volatilized with decomposition at a white heat. When heated in the presence of silica, a lead silicate is formed as in the "slag roasting" of siliceous galena. It is reduced by carbon and iron, and it reacts with PbS giving metallic lead.

Lead sulphate is only slightly soluble in water, but is soluble in various saline solutions, especially in those of ammonium tartrate and acetate.

Lead Carbonate, $PbCO_3$.—This is found native as cerussite. It loses its CO_2 at 200° C. It is completely reduced by carbon and carbon monoxide.

Lead Sulphide, PbS.—This occurs native as galena, the chief ore of lead.

It fuses at a strong red heat (about 1,114° C.), and becomes so fluid that it will filter through a clay crucible without corroding it ; and it penetrates the fire-brick lining of furnaces. If air be excluded, it volatilizes unchanged, and its volatilization is promoted by furnace gases. It readily mixes with Ag_2S, Cu_2S, ZnS, and FeS, forming the mattes produced in smelting ores containing them. Iron decomposes it more readily than any other metal, but the iron sulphide formed always retains some undecomposed lead sulphide. Similarly, when sulphide of lead is heated with iron oxides and carbon it is quickly reduced.

A basic ferrosilicate, $4FeSiO_6[4FeO, SiO_2]$, will also decompose galena readily, while the monosilicate, $2FeSiO_4[2FeO, SiO_2]$, has little effect.

Copper and zinc only partially decompose it.

Galena is partially decomposed by both lime and baryta. If carbon is absent, the reaction is probably (*Collins*)—

$$4PbS + 4CaO = 3CaS + CaSO_4 + 4Pb.$$

Or, if carbon is present (*Berthier*)—

$$2PbS + CaO + C = Pb + (PbS, CaS) + CO.$$

When lead sulphide is roasted it yields PbO and $PbSO_4$. The proportion of lead sulphate varies with the temperature at which the roasting has been conducted ; a low temperature and slow roasting tending to produce more sulphate than a high temperature and quick roasting. More sulphate, too, is formed when iron pyrites is present. When lead sulphide is heated to a bright red heat with lead oxide or lead sulphate, the following reactions, on which a very important process of lead extraction is based, take place—

1. $PbS + 2PbO = 3Pb + SO_2.$
2. $PbS + 3PbO = 3Pb + PbO + SO_2.$
3. $2PbS + 2PbO = 3Pb + PbS + SO_2.$
4. $PbS + PbSO_4 = 2Pb + 2SO_2.$
5. $PbS + 2PbSO_4 = Pb + 2PbO + 3SO_2.$
6. $PbS + 3PbSO_4 = 4PbO + 4SO_2.$

From these equations it will be seen that, in order to obtain the whole of the lead as metal, the proportions given in Nos. 1 and 4 must be adhered to. A low temperature must be kept during the roasting operation, after which it must be rapidly raised to bring about the reactions.

Commercial Lead and its Impurities.—There are two chief classes of lead in the market—viz., soft lead and hard or antimonial lead. The first is obtained from pure ores, from the refining of argentiferous lead, and by electrolytic refining.

The sources of the second are antimonial ores, especially in Spain, the by-products of the refining processes, and the smelting of slags.

Soft lead is used for the manufacture of sheets and pipes, the preparation of white lead, and of solder and pewter.

A certain amount of hard lead is used for making bearing metals and other alloys, and generally it is used for purposes where a common metal will suffice.

The impurities present in soft lead are almost invariably in very small amounts, the total percentage rarely exceeding ·02 or ·03 per cent. in the best brands, and sometimes being as low as ·01 per cent. The chief impurities are Cu, Sb, Bi, Fe, Ag, and Zn.

Analyses of typical brands of refined lead are given in the following table. The analyses were made in the Technical Analysis Department of Osaka, Japan:—*

	Selby, San Francisco.	Electrolytic. Trail, Brit. Col.	English.	English Chemical.	Broken Hill Proprietary.	English. Enthoven.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Lead, . .	99·9579	99·9890	99·9762	99·9693	99·9853	99·9851
Insolubles, .	0·0040	trace	trace	trace	trace	trace
Bismuth, .	0·0300	none	0·0046	trace	none	0·0048
Cadmium, .	trace	none	0·0002	0·0007	trace	trace
Nickel, . .	0·0001	trace	trace	0·0003	none	trace
Cobalt, . .	none	none	trace	trace	trace	trace
Silver, . .	0·0010	0·0025	trace	0·0020	0·0009	0·0015
Manganese, .	0·0008	none	0·0003	none	none	none
Copper, . .	none	0·0003	none	0·0097	none	none
Antimony, .	none	none	0·0137	0·0149	0·0108	0·0160
Tin, . .	0·0004	0·0007	none	none	0·0004	none
Arsenic, . .	0·0024	0·0020	0·0090	0·0002	none	none
Zinc, . .	0·0003	0·0002	trace	trace	0·0001	trace
Iron, . .	0·0027	0·0053	0·0039	0·0029	0·0025	0·0026

Soft lead, in fact, prepared by commercial processes only, is one of the purest metals produced in metallurgical operations on a large scale. Its purity is only approached by highly refined gold and silver bullion.

This great purity is due to the ease with which lead oxide is formed, and to the property the oxide possesses when fused of dissolving readily the oxides of contaminating metals.

The purest soft lead is preferable to every other description of lead for vitriol chambers, towers, tanks, pipes, and all other instances where the temperature can rise but moderately and certainly never over 200° C. (*Lunge*).

Effects of Contaminating Metals—*Copper.*—Copper does not form a homogeneous alloy with lead.

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* *Eng. and Min. Journ.*, June, 1907.

If copper and lead are melted together in equal parts, or, in any other proportion, in which the lead is in excess, and the mixture be stirred well and cooled rapidly, and the mass be then cautiously heated beyond the melting point of lead, but below the melting point of copper, much of the lead will trickle out, and leave the copper in a spongy form. The lead takes with it a little copper, nearly all the silver, and also any bismuth which may have been present. On this behaviour the old liquation process for the separation of silver from copper was based. Copper is a common impurity in lead, but rarely in sufficient amounts to interfere with the rolling of the metal.

For the manufacture of white lead or glass, not more than 0·0014 per cent. (*Hampe*) should be present.

For certain chemical purposes, for example boiling pans for sulphuric acid, the presence of copper in quantities up to 0·05 per cent. may be an advantage.

Antimony.—Lead is rendered sensibly harder and less malleable by the presence of antimony, but if under 0·005 per cent., according to Hampe, there is no apparent effect.

According to Lunge, about 0·2 per cent. antimony may be useful in sulphuric acid tanks and apparatus when the acid is always cold, but more recently, it has been considered objectionable.

Bismuth.—The Parkes process does not, like the Pattinson process, remove bismuth from lead.

In the proportions usually present it has no effect on the physical properties of the metal, and up to 0·075 per cent. it is without effect on white lead.

Iron.—The physical properties of lead are not affected by the small quantity usually present.

Silver.—Silver alloys with lead in all proportions, but, as we shall see later, none of the alloys is quite homogeneous. In the lead of commerce only small quantities are present, usually 5 to 15 dwts. per ton.

According to Baker, 1·7 ozs. of silver per ton gives a reddish tinge to white lead, but 0·15 oz. has no effect.

Zinc.—Lead is rendered hard and less malleable by zinc, but the quantity present in the refined metal is insufficient to have any effect. When lead and zinc are melted together they separate on cooling (see p. 232). The behaviour of zinc and lead will be further considered under the Parkes process.

Arsenic.—Lead readily alloys with arsenic. Arsenic hardens the metal and increases its fluidity. When present in small amounts it facilitates the formation of spherical drops, and this property is utilized in the manufacture of shot for sporting purposes. Two samples analysed in Dr. Percy's laboratory contained—

No. 1 shot, ...	As 0·133	per cent.
	Cu 0·30	,,
No. 6 shot, ...	As 0·116	,,
	Cu 0·28	,,

Chief Industrial Alloys of Lead.—On the property which lead possesses of alloying with silver and gold, the extraction of these metals from their ores by smelting is based. The alloys of lead which are in most common use are those with antimony, and especially with antimony and tin, such as the antifriction and type metals, and with tin alone, as pewter and solders.

Lead is largely used for sheathing of cables, etc., and, owing to its low fatigue limit such sheathing when made of pure lead, being subject to vibration, has frequently failed. The most satisfactory method of raising the fatigue limit is to alloy the lead with 0·5 per cent. cadmium or with cadmium together with tin or antimony to a total of 0·5 per cent.*

In the table which follows is given the approximate composition of the alloys of lead which are of chief importance in engineering and other industries.

CHIEF INDUSTRIAL ALLOYS OF LEAD.

Description.	Pb.	Sb.	Sn.	Cu.	
Type metal, best for special use,	50	25	25	..	Law.
,, ...	60	30	10	..	,,
,, ...	70	18	10	2	
Stereotype metal, . . .	82·0	14·8	3·2	..	
Bearing metal for heavy work,	84	16	..	..	
,, Pennsylvanian Railway, .	87	13	..	..	
,, for light work, .	60	20	20	..	
"Magnolia" and "Tandem" metal, ...	77·7	16·8	5·9	..	Thurston.
Plumber's solder, . . .	50	..	50	..	Hughes.
	66·6	..	33·3	..	
Tinsmith's solder, . . .	40	..	60	..	Hughes.
	33·3	..	66·6	..	
Pewter, English, . . .	20	..	80	..	
,, French, . . .	18	..	82	..	

Ores of Lead.—The ores of lead are divided into two classes—namely, "sulphide ores" and "oxidized ores." The former consists of galena, which is generally more or less mixed with pyrites and other sulphides, etc.

The latter are called "carbonates" in America, and under this term are included not only cerussite, but also anglesite and pyromorphite. In America ores containing lead are often termed "leady" ores, and those containing no lead "dry" ores.

All the ores of lead contain silver. When they contain sufficient silver to pay for its extraction they are designated as "argentiferous"; when in less quantity "non-argentiferous." In every case, when smelted, the silver in the ore passes into the lead reduced, with the exception of a small quantity, which may be retained in the slag, or, as we shall see later, in the case of mixed ores, in a regulus or a speise, which sometimes accompanies the reduced lead.

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* Beckinsale and Waterhouse, *Journ. Inst. of Metals*, 1928, vol. xxxix., p. 375.

Galena, PbS ; 86·6 per cent. Pb. The chief ore of lead.

When only contaminated with vein matter, such as calcspar, quartz, barytes, or clay slate, etc., the ore may be concentrated by simple mechanical dressing operations, and the dressed mineral is then ready for treatment by the smelter.

An extremely poor ore of this class can thus be concentrated ; for example, in Rhenish Prussia a 2·5 per cent. ore in a soft sandstone is economically worked.

Too often, however, it is mixed, more or less intimately, with other sulphides, iron and copper pyrites, zinc blende, and with mispickel, which cannot always be separated economically by mechanical treatment.

Galena always contains silver, and almost always in quantities which it will pay to extract. Gold also is always present, but generally only in very small amounts, although 15·2 ozs. gold per ton has been reported in galena at Sonora (Mexico). The silver is rarely present as native silver, but usually as argentite (silver sulphide) or other silver-bearing minerals. The argentite may be in intimate isomorphous admixture with the galena. Or, it or the other silver minerals may be present merely in association with the galena, as distinct minerals in the cleavage planes.

The state in which the silver exists is of great importance as regards the dressing of the ore.

If the silver minerals are in isomorphous combination, the loss of the silver in dressing will be proportionate to the loss of lead.

If, however, the silver minerals are only in association with the galena, the loss of silver may be very great, as these minerals are brittle and light in comparison with it, and will be washed away as slime. Therefore, any black fine slime seen floating on the water from the jigs should always be collected and assayed for silver.

When galena is associated with cerussite, the silver may be present as chloride, and in such case dressing by water is out of the question.

At Handa, Japan, an ore consisting of argentiferous galena, cerussite, iron pyrites, zinc blende, and copper pyrites, in a gangue of quartz and calcspar, rather poor in lead, had been long worked by native methods. The ore had been concentrated by washing, and then been smelted, until the lode became too poor to work. The tailing amounted to over 40,000 tons. When the mine was reopened, to be worked by European methods, and some of the heaps which contained most galena were rewashed, a peculiar-looking mud was noticed near several of them. This, on assaying, was found by the author to contain up to 2,775 ozs. of silver per ton, and the poorest parts of the heaps 26 ozs., all in the state of chloride.

It has often been said that fine-grained galena is richer in silver than the coarse-grained varieties. This is by no means always true, as Dr. Percy has shown.* When galena is much intermixed with other sulphides, the ore is often richer in silver than in simple ores containing galena alone. It is then very necessary, in fact, imperative, to ascertain whether the silver is contained wholly in the galena or partly and to what extent in the other sulphides. This is especially advisable in dealing with an ore poor in galena and containing iron pyrites and zinc blende which we might be tempted to concentrate in order to smelt it for lead. In illustration of this may be quoted an example from Leadville, where the galena in the ore contained 41½ ozs. silver per ton, the zinc blende 94½ ozs., and the pyrites 4½ ozs. In this case, it is evident that to concentrate the galena, for smelting, and throw away the zinc blende, would result in the loss of a large proportion of the silver.

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* Percy, *Metallurgy of Lead*, p. 97.

The chief deposits of galena in Great Britain are in Derbyshire, N. Wales, and Lanarkshire, but they are small and unimportant compared with those in other countries. It occurs in special abundance in Idaho, Missouri-Kansas, Utah, Colorado, and other States in N. America, in Spain, Sardinia, Greece, and New South Wales, and to a lesser extent in Germany.

At Broken Hill (N.S.W.) there are extensive deposits of an ore consisting of galena and a variety of zinc blende so intimately mixed that the ordinary methods of dressing have to be supplemented by flotation processes, in order to obtain the former free from objectionable proportions of zinc, and the latter from objectionable proportions of lead, so that they may each be suitable for metallurgical treatment.

The zinc mineral is popularly referred to as blende, but there is practically no real blende in this ore; the mineral is actually marmatite in which the zinc is partly replaced by isomorphous iron and manganese (*Moulden*).

Cerussite (Lead carbonate, $PbCO_3$).—77·5 per cent. Pb when pure. It occurs in the outcrops and gossans of galena deposits, and it and anglesite, lead sulphate, are the products of the oxidation of the sulphide. Generally some anglesite and also galena are associated with it.

In estimating the value of deposits of carbonate ore, it is important to remember that the ratio of silver to lead in these is much more variable than in deposits of galena. The silver is mostly present as chloride, but sulphide and native silver also occur.

Ores in which cerussite occurs cannot be satisfactorily concentrated by wet dressing processes, as considerable losses in lead and silver may be incurred owing to its tendency to pass away as slime. Several important deposits of cerussite, as at Laurium (Greece) and Leadville (Colorado) have been practically exhausted. At present it occurs chiefly at Carthagena, and Linares (Spain), Utah, one or two mines in Mexico, and at Broken Hill (N.S.W.).

Anglesite (Lead sulphate, $PbSO_4$).—It usually occurs in association with galena and cerussite, and is unimportant as an ore of lead.

The following minerals are of less importance than those mentioned above, as they rarely occur in sufficient quantities to be considered ores.

Pyromorphite, $3Pb_3(PO_4)_2 + PbCl_2$; mimetesite $3Pb_3(AsO_4)_2 + PbCl_2$.—They occur in the upper decomposed portions of galena deposits. The former has been worked as an ore in Derbyshire under the name of "linnets," from its linnet-like colour.

Vanadinite, $3Pb_3(VO_4)_2 + PbCl_2$.—Chief locality, Spain. It was until recently the chief commercial source of the metal vanadium, which is used in the manufacture of certain steels.

Other lead minerals which, however, cannot be considered as ores, as they rarely occur in large quantities, or otherwise than associated with ores of lead, are the following:—

Crocoisite, $PbCrO_4$; *Wulfenite*, $PbMoO_4$; *Stolzite*, $PbWO_4$; *Mendipite* $PbCl_22PbO$; and sulphantimonides, such as *Jamesonite*, *Bournonite*, etc.

LEAD SMELTING.

Classification of Smelting Processes.

1. **Roast Reactions Process.**—This is founded on the fact that when lead sulphide is intimately mixed either with lead oxide or lead sulphate, or with both, in such proportions that the oxygen and sulphur in the mixture are in the same proportions as those elements exist in sulphur dioxide, and the mixture is heated to a certain degree, complete reduction of the lead takes place, the oxygen and sulphur entering into combination, and escaping as sulphur dioxide (see p. 177).

2. **Roast Reduction.**—This process is carried on by roasting and subsequent reduction of the oxidized products wholly or mainly by carbonaceous matter.

3. **Iron Reduction Process sometimes called the Precipitation Process.**—In this process metallic iron, or an oxidized compound of iron, which will yield metallic iron during the process, is employed to aid in the desulphurization.

In some cases, two or even all of the above processes are combined.

Another practical classification is one which is based on the kind of furnace in which the smelting operations are conducted. It is as follows :—

1. Smelting in reverberatory furnaces.
2. Smelting in hearths.
3. Smelting in shaft furnaces.

Smelting in Reverberatory Furnaces.—The only process now carried on in reverberatory furnaces is the "roast-reactions" process. The "iron reduction" process formerly carried on in reverberatory furnaces, and known as the "Cornish" or "flowing" process is no longer in use for ores, owing to its heavy expenses and loss of metal; although it is sometimes employed for slags. The furnace chiefly employed is the Flintshire furnace, or a modification of it. The advantages of smelting galena by the "roast-reactions" process in a reverberatory furnace are :—

1. The ore is treated in a raw state.
2. The furnace and appliances are less costly than a shaft furnace, with its engine, blowers, etc.
3. Common slack can be used as fuel.
4. The greater part of the lead is quickly extracted in a pure state.
5. Loss by volatilization is comparatively small.
6. The greater part of the silver, if the ore is argentiferous, is obtained in the lead, but little remaining in the residue.
7. Purity of the lead obtained.

Its disadvantages are, that it is only suitable for rich and pure ores, and requires much labour. The characters which an ore should possess to be suitable for the process are the following :—

1. The ore must not contain less than about 58 per cent. lead.
2. The ore must not contain more than 4 per cent. silica, even 1 per cent. being injurious, as it forms lead silicates, which are extremely fusible, and

coat the particles of ore, preventing them from being oxidized; and also because lead silicates are not reduced at the temperature of the furnace.

3. It must not contain more than about 10 per cent. of iron pyrites, blende, or calcspar.

In small quantities, however, iron pyrites assists the reaction both in the roasting and subsequent fusion. Any iron sulphate formed at first will give up SO_3 later, and thus the formation of lead sulphate is promoted. In the "setting up," too, the iron oxide tends to stiffen the charge.

When much iron pyrites is present, there is a tendency for some of the FeS to run down as a matte containing lead sulphide.

Blende becomes converted into ZnO and $ZnSO_4$, some being unoxidized, and up to 4 to 5 per cent. is said to assist the roasting process, while 10 per cent. or more retards it, the charge requiring then to be frequently "set up."

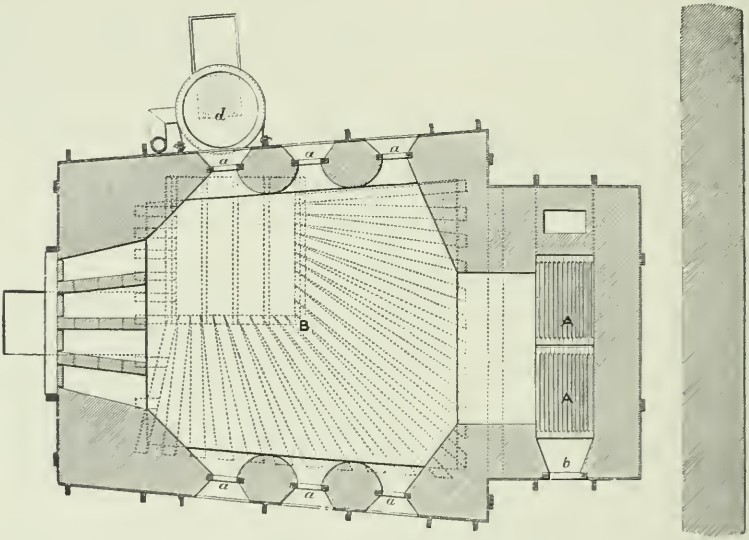

Fig. 59. Flintshire Furnace, Couëron*—Horizontal Section on CD.

Calcspar diminishes the fusibility of the charge, and if not more than 10 or 12 per cent. is present this is an advantage. With larger quantities the reactions in running down the charge are retarded.

4. Copper pyrites, and barytes with fluorspar, must be present only in small quantities.

Copper pyrites acts like iron pyrites, and besides some copper passes into the lead. Barytes and fluorspar when present together make the charge too fusible.

5. Antimony should be present only in the smallest possible quantities, as it is the most injurious of all the metals.

The volatility of its oxide and sulphide causes losses of both lead and silver, and their fusibility retards the roasting by causing the charge to cake.

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* Collins, *Lead*, p. 32.

Moreover, it enters the lead, producing *hard* lead.

6. Arsenic should, as far as possible, be absent, as it resembles antimony in its injurious effects.

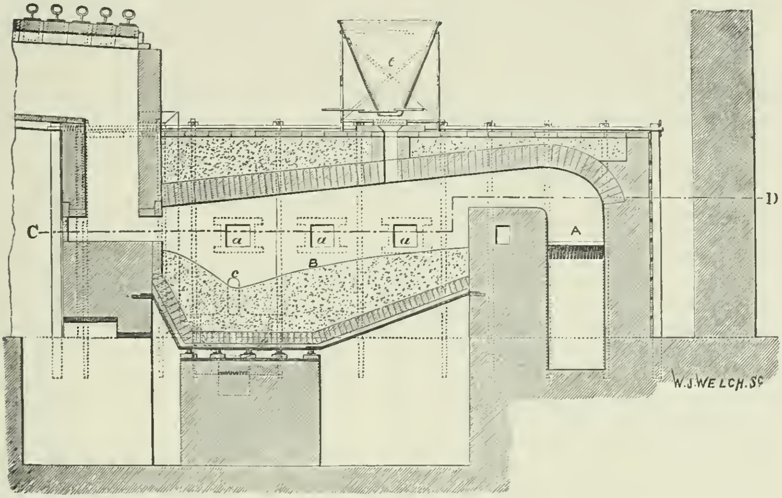

Fig. 60.—Flintshire Furnace, Couëron *—Longitudinal Section

The reverberatory furnace, which is chiefly used in this country, is the Flintshire furnace.

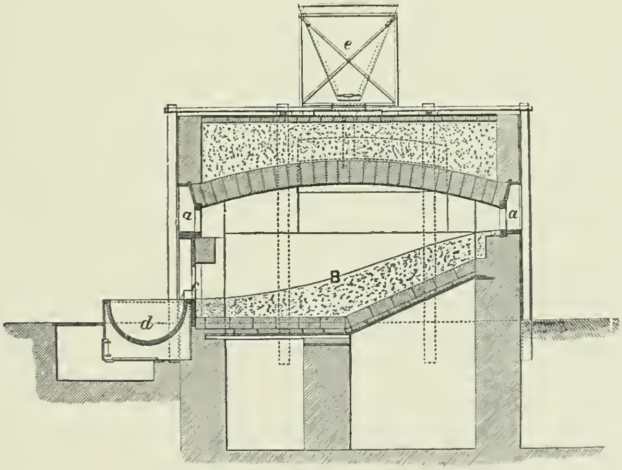

Fig. 61.—Flintshire Furnace, Couëron †—Transverse Section through Taphole.

The Flintshire Furnace (Figs. 59, 60, and 61).—The hearth or working bed is always built over a vault, to avoid loss of lead in the foundation. It is supported on iron rails or plates, over which, in the former case, a course of fire-tiles is laid, and upon these a course of 9-inch fire-bricks, set on edge. If plates are used only fire-bricks are required. The true working bottom is usually made of the grey slag produced in smelting. The slag is broken into pieces of the size of road metal, and is thrown into the furnace, which has been heated to redness, and spread over the fire-brick bottom. It is then melted and run down into the well of the furnace, where it is allowed to cool until it is pasty, in which state it is worked by rabbles over the fire-brick bottom into the required shape shown in Figs. 60 and 61.

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* Collins, *Lead*, p 32.

† Collins, *op. cit.*, p. 33.

The bed is about 10 feet long, 9 feet 6 inches broad at the fire-box end, and 8 feet at the other. The fire-box measures 6 feet by 2 feet by 1 foot 6 inches, and is specially made shallow in order that the temperature may be rapidly raised when necessary. The fire-bridge is air-cooled.

The outer and cooler parts of the furnace may be built of red bricks, the other parts of fire-bricks, and the whole is generally enclosed with cast-iron plates firmly bound with buckstays and tie-rods.

The flue at the end of the furnace, which is divided into three or four channels, is not set on the middle line, in order that more flame will pass over the highest part of the bed than over the well.

There are six working doors.

A hopper of wrought iron, capable of holding a whole charge, is set over an opening in the arch of the furnace.

A cast-iron pot, sometimes heated by its own fire, is set in front of the taphole, which should be below the third door. The taphole is best in this position, as it then allows the maximum area of bed for roasting, and the lead is collected in the coolest part of the furnace. It is usually closed with lime in Flintshire, and not with fire-clay.

The Process.—The usual charge for a furnace in North Wales is 29 cwts. of ore, containing from 75 to 80 per cent. of lead, by the iron crucible assay, and three charges are worked off in twenty-four hours, two furnacemen and a labourer being required. Each charge yields about 1 ton of lead, and about 3½ to 4 cwts. of grey slag, containing 50 per cent. or rather more of lead by crucible assay. The furnace being red hot from the preceding charge, the ore is charged in through the hopper and spread over the whole of the upper part of the bed in front of the fire-bridge, flue and side, care being taken to prevent any from falling into the lower part or well of the furnace. It is frequently stirred and turned over with rabbles for two or three hours, in order that a sufficient amount of the PbS be oxidized to PbO and $PbSO_4$, the temperature being kept as high as possible, but clotting must be avoided.

The temperature is then raised, and the charge melted down into the well. The PbO and $PbSO_4$, which have been formed in the roasting, react with the unoxidized PbS during this stage, and the reduced lead accumulates in the well.

$$PbS + 2PbO = 3Pb + SO_2.$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

A few shovelfuls of lime are now thrown in, to thicken the slag and unreduced ore which float on the molten lead.

This is then "set up"—*i.e.*, it is pushed up to the top of the bed, allowed to cool sufficiently to allow it to be broken up, and worked about to oxidize more PbS. This lasts for about an hour, when the temperature is again raised, and it is melted down. If the ore is pure, the "setting up" and melting down may have to be repeated only once more, but if impure several times. The temperature is then raised, and the charge thoroughly melted.

The slag is thickened with a little lime and raked out in a pasty condition through the doors in the back of the furnace—*i.e.*, the side opposite the taphole. The taphole is then opened, and the lead run out into the cast-iron pot in front. The lead is skimmed, the skimmings thrown into the furnace, and the metal when sufficiently cool laded into cast-iron moulds to form the pigs of commerce. The bed of the furnace is repaired, and a new charge dropped in as before.

The time occupied in working off a charge is about eight hours. Sometimes the grey slag is not raked out until the lead is tapped, and in Derbyshire, when the vein-stuff is very fusible, it is run out through the taphole. The grey slag is a variable mixture of lead sulphate, oxide, and much silicate and lime, with shots of metallic lead, and contains about 50 per cent. Pb. The action of the lime is chiefly mechanical, but possibly it may help to set free PbO from silicates formed during the melting down of the charge.

The grey slag, in Flintshire, is smelted in a reverberatory furnace termed a "flowing furnace," which in construction closely resembles that used in smelting the ore.

The reducing agents employed are iron and "culm" (small coal or anthracite), and the slag produced consists for the most part of ferrous and calcium silicates. The grey slag mixed with "culm" and scrap iron is charged into the furnace, which is hot from the working of a previous charge. Old broken Pattinson pots, or any available iron scrap, are used, the larger pieces of iron being put in here and there in the charge. The temperature of the furnace is urged and the charge is fired on for six hours, after which the taphole is opened, and the lead and slag tapped out into a cast-iron pot in front. The lead accumulates in the pot, and the excess of slag overflows and runs into a long shallow channel, about 16 inches to 18 inches broad, where it solidifies. The slag contains only about 2 per cent. lead, and is thrown away, except that in and near the pot.

The lead is termed "slag lead," and is hard and impure, containing antimony, copper, and other impurities, which were present in the ore.

The Silesian Process.—This process may be considered as a modification of the English (Flintshire) process, from which it differs in the use of a larger furnace, a lower temperature, the addition of oxidized materials at one stage of the operations, and in obtaining the lead at several tappings. The loss of lead by volatilization is said to be lower than in any other process, and the lead produced to be purer. The ores should contain about 70 per cent. lead as galena.

The furnace employed is shown in Figs. 62 and 63. There are four working doors on each side, the cast-iron pot for receiving the lead being opposite one of the end doors. The bed or hearth is 16 feet 6 inches long and 9 feet broad, and slopes gradually towards the well, which is at one side of the end next the flue, the coolest part of the furnace. The working bottom is made of the residue left after the smelting process mixed with lime. It rests on a layer of brasque (clay mixed with ground coke), which is well beaten down upon a course of red brick laid on a thick bed of sand. The fire-bridge is air-cooled.

The Process.—About 2½ to 3½ tons of the ore are dropped through the hopper in the roof into the furnace, which is red hot from a previous charge, and carefully roasted at a low temperature with frequent rabbling for three or four hours, to oxidize lead sulphide. Then an addition of 10 to 12 cwts. of roasted ore, various residues from the works containing lead oxide, and sometimes some lead carbonate ore, is made to assist in the reaction upon unaltered lead sulphide. The temperature is now raised, the reaction stage begins, and lead trickles into the well. The ore is not allowed to melt, and as it softens it is thickened by throwing in lime, the further oxidation of lead sulphide being promoted by rabbling. The charge now cools down so that lead ceases to flow. The temperature is then again raised, when more lead

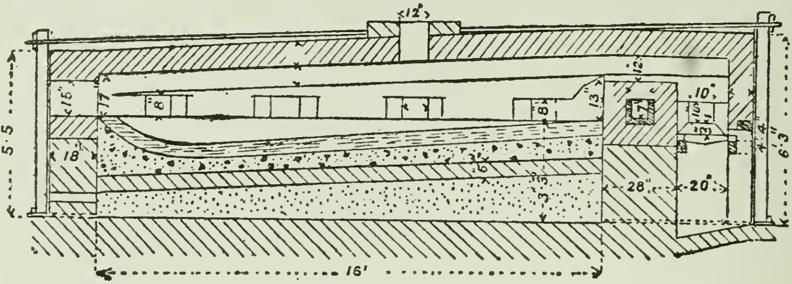

Fig. 62.—Silesian Furnace *—Longitudinal Section.

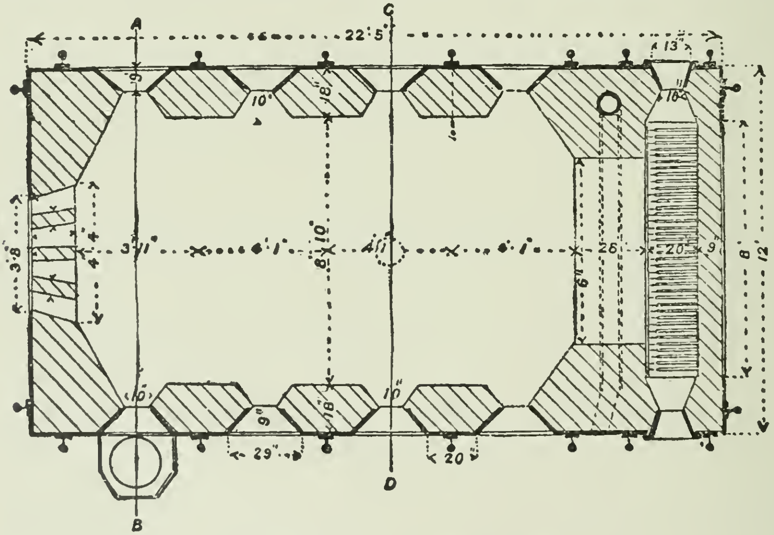

Fig. 63.—Silesian Furnace †—Plan.

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* Collins, *op. cit.*, p. 41.

† Collins, *op. cit.*, p. 41.

runs down, and again the charge is rabbled and cooled. This alternate oxidation and heating goes on every $1\frac{1}{2}$ to 2 hours for about 7 hours, when no more lead can be extracted. The first lead is tapped out about three hours after the beginning of the reaction stage. It is very pure, and also richer in silver than that from the subsequent tappings which are made about every hour and a half.

After the final tapping the residue is raked through an opening in the side of the hearth, not shown in the figure, into a slag pot below. It contains from 40 to 56 per cent. lead, and is smelted in a small shaft furnace.

The time required for the operation is eleven to twelve hours, and 60 to 65 per cent. of the total lead in the ore is obtained as metal. The reactions are the same as in the English process.

Lead Smelting in Hearths.—A typical hearth is the Scotch ore hearth, formerly in use at Leadhills, Lanarkshire, and also in Derbyshire and Yorkshire. It has been modified in America by substituting water-cooled or water- and air-cooled jackets for the massive cast-iron blocks which form its sides.

The reactions are those of the "roast reactions," processes we have just considered, but differs from them in that the roasting and reduction go on at the same time. It is suitable for remote places where coal is dear, labour cheap, the output of the ore irregular, and water power is available for the blast.

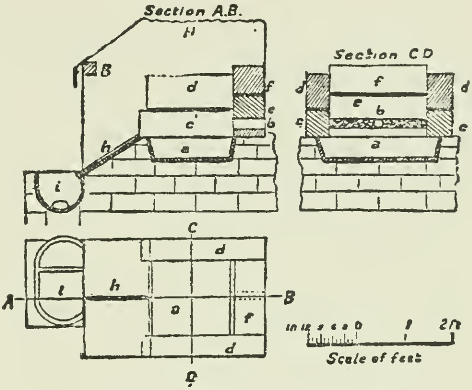

Fig. 64.—Scotch Ore Hearth.*

It requires less fuel than a reverberatory furnace, its first cost is much less, and a large quantity of pure lead is obtained at once. On the other hand, it is unsuitable for galena rich in silver, on account of the heavy volatilization losses, and the cost per ton of ore treated is higher than in a reverberatory.

One of the furnaces used at Leadhills is shown in Fig. 64. It consists of a cast-iron trough or sump set in brick or stonework. On this sump the hearth proper is built on three sides, with massive rectangular iron blocks called "stones," the front being left open.

In front of the sump is a sloping cast-iron work plate, with a turned-up edge and a groove running across it from the edge of the sump for the passage of the lead. The pot for receiving the lead is in front of the work plate. It is 2 feet 6 inches long and 12 inches wide. Near one end is a partition going nearly to the bottom, to keep back scum and ashes in the larger division, and allow only clean lead to flow into the smaller, whence it is ladled into moulds. The blast is supplied by a Roots' blower, driven by a water wheel, and passes into the hearth through a tuyere in the back of the furnace.

The Process.—The ore must be rich in lead; that treated at Leadhills is concentrated up to 77 per cent. The furnace being in work, the hearth is full of molten lead, with the charge of ore and fuel which is being worked floating upon it. In front is a pile of ore, one of fuel and another of lime.

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* Collins, *op. cit.*, p. 51.

The workman, from time to time, introduces a rabble into the charge, stirs it up, removes a portion on to the work plate, and examines it. Any fragments of slag he throws aside, the residue, half-decomposed ore, he returns to the hearth, after throwing some lime upon it, together with some fresh ore; about 20 to 25 lbs. mixed with 1½ to 2 per cent. lime, also some coal. This operation is repeated about every five minutes. The coal is thrown chiefly in front of the tuyere, and the charge is manipulated with a rabble, so that the blast shall be well distributed through it. During these operations the lead oxide formed reacts with the unoxidised sulphide, lead is freely reduced, and flows down the groove in the work plate into the lead pot.

Each hearth, when treating ore containing 77 per cent. lead, yields on an average 1 ton of lead per shift of six hours, and two workmen are required per shift.

The grey slag contains 35 to 40 per cent. of lead; sometimes more. It is smelted in a low blast furnace. One of the chief disadvantages of the ore hearth process is the loss of lead by volatilization. Condensing chambers for the fumes are in use in this country, but they are not very satisfactory; in America, however, at one or two works, bag-house plants have been erected, and the fume collected utilized for pigments.

One of the chief American modifications of the Scotch ore hearth is in use at the works of the Federal Lead Company, Ill.,* where there are twenty hearths. The sump of each furnace measures 4 feet by 2 feet by 1 foot, and contains about 1 ton of lead. The two sides and back wall consist of cast-iron water-jackets, with a waterspace only 1 inch wide. The furnaces stand in a single row, and are supplied with low-pressure blast from a main which runs behind them. Branches from this main deliver the air into a wind chest at the back of each furnace, and from this the blast passes into the furnace by eight 1-inch pipes. Over each furnace is an iron hood, leading into a common flue, through which a fan draws the fumes and gases, and forces them into a bag-house. The ore smelted is galena which has been concentrated up to 65 to 70 per cent. of lead. About 70 per cent. of the lead contained in the ore is obtained as metal. When working to the full capacity, with ore containing 80 per cent. of lead and over, the twenty furnaces can produce about 200 tons of lead in twenty-four hours, with a coke consumption of 8 per cent. of the weight of the ore. The slag and bag-house dust, etc., are smelted in a water-jacketed blast furnace.

The Jumbo or Moffet Hearth.—It produces much less metallic lead than the other hearths, but a larger quantity of fume, and has hence been used for the manufacture of pigment.

The hearth box or sump is a simple iron trough, 4 feet long, 2 feet 6 inches wide, and 10 inches deep, supported on four short iron columns. It is divided longitudinally by a hollow iron box, in which there is a hole near the bottom for the lead to enter. On the top of this is a water box surmounted by an air chest. The furnace thus consists of two long hearths placed back to back.

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* *Eng. and Min. Journ.*, 1906.

Upon each long side of the hearth box there is a water box, and on each short side an air box. The working part of the hearths is thus water- and air-cooled.

Air is supplied from the air chest to the 14 tuyeres, 7 for each inner side of the hearths, by pipes leading through the water box.

The fumes are led away by a sheet-iron hood connected with a system of flues, a dust chamber, and a bag house.

The ore hearth, in the form of the water-jacketed American, and the Jumbo hearth, is in extensive use in the Missouri lead belt, where large quantities of non-argentiferous galena concentrate are produced. Its use is, however, restricted to non-argentiferous galena containing over 68 per cent. of lead, and for this class of ore it is contended that it can do cheaper work than the ordinary blast furnace.

A radical improvement in the hearth has been made by Mr. W. E. Newnham at the works of the St. Louis Smelting and Refining Company, at Collinsville, Illinois,* in which mechanical rabbling replaces that formerly done by hand.

The hearth has also been enlarged. The length of the old hearths was limited to from 4 to 5 feet, and required two men working on 8-hour shifts, the length of the new hearth is 8 feet, and while it requires the same number of men, it treats two and a half times the amount of ore. The work too is light, and the workmen are less exposed to lead fumes.

The rabbling machine is hung from an electric carriage, which travels on an overhead track, and the rabbling is done in one direction only. The machine being at rest at one end of the furnace, a lever is pulled, the machine starts, the rabble arm describing a motion similar to that of the hand rabble. When the rabble arm is withdrawn from the fire, a ratchet wheel moves the carriage forward about 4 inches for the next stroke. This motion is repeated until the other end of the furnace is reached, when the machine stops, withdraws the rabble from the fire, and returns to its original position. Two men, a charger and a helper, work the furnace. The helper follows the rabble, pushing back the loose charge with a long-handed shovel and picking out the grey slag. The charger comes close behind him, spreads a thin layer of ore on the charge as fast as it is shovelled back, adding coke breeze as needed, and transferring grey slag to the water box. By the time the trip down the furnace is completed, the end first charged is ready for the rabbling machine. In the following table it will be seen that the improved hearth with mechanical rabbling gives a much higher extraction of metallic lead than the old hearth, with a decrease in the amount of dust and fume produced and fuel used.

The following table is a comparison of the two types of hearth, operating side by side on the same ore, showing the average results per 8-hour shift over a period of four weeks, the labour being the same on each type :—

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* *Eng. and Min. Journ.*, Oct., 1915. Abstract of paper by W. E. Newnham, *Bulletin* A.I.M.E.

Comparative Results on Newnham and Hand Hearth.

Ore charged, galena concentrates, containing 72·5 % lead, and 15·1 sulphur.

	Newnham Hearth. Lbs.	Hand Hearth. Lbs.
Dry ore charged,	13,179	5,091
Lead contents,	9,554	3,691
Pig lead made,	6,443	2,030
Grey slag made,	3,318	1,329
Per cent. of coke breeze used,	3·6	8·8
Rabble trips per hour,	37·2	..

Percentage of Total Lead in Products.

Pig lead,	67·44	55·00
Grey slag,	15·18	16·20
Dust and fume,	17·38	28·80
	100·00	100·00

Several plants having a capacity of 100 tons of concentrate per day are now in operation.

Lead Smelting in Blast Furnaces (Shaft Furnaces).—All ores which can be smelted can be treated in the shaft furnace.

All ores containing over 4 or 5 per cent. SiO_2 must be so treated, also the ores already considered as unsuitable for the reverberatory furnace. The furnace is specially suitable for impure pyritic ores.

If the ore is a sulphide, or a mixture of sulphides, it must be first roasted ; on the other hand, if the ore consists of cerussite or a mixture of galena and cerussite, the latter being in excess, it is smelted direct.

The Roasting of Lead Ores.—Ores containing 12 per cent. sulphur or more were generally roasted unless they were rich in silver.

It may be mentioned here that in lead-smelting practice, in all important works, the ore is treated for the purposes of desulphurization by either the Huntington-Heberlein or the Dwight-Lloyd systems (see pp. 196, 198), by which it is also sintered into a form suitable for smelting in the blast furnace. The older methods of roasting now to be described are in but limited use, and are being discontinued.

Ores with 100 ozs. silver per ton are, as a rule, not roasted, on account of the loss of silver which may be incurred ; some metallurgists even put the limit at 50 ozs. Concentrate from the milling of gold ores is always roasted.

The object of roasting is to drive off as much as possible of the sulphur, and also of the arsenic if present, and thus reduce the amount of matte and speise produced on smelting. In roasting pyritic ores containing copper, however, enough sulphur must be left to form a matte with the copper, but the blast-furnace charges of cupriferous lead ores should be arranged so that the production of matte should be about 5 per cent., and not above 10 per cent., otherwise the loss of silver in the slag will be increased.*

The chief reactions that occur in roasting a pyritic lead ore are expressed in the following equations :—

1. $FeS_2 = FeS + S.$

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* Hofman, *Lead*, p. 156.

The iron pyrites gives off one atom of sulphur on simple heating, part of which burns to SO_2 and part becomes SO_3 by contact with the porous charge and furnace brickwork, and with oxygen in the air.

$$2.\ 3FeS + 11O = Fe_2O_3 + FeSO_4 + 2SO_2.$$

Some iron sulphate is always formed, and the more when the temperature is low and the roasting slow.

As the temperature rises it is decomposed—

$$3.\ 2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

Copper sulphide is similarly oxidized—

$$4.\ 3CuS + 9O = Cu_2O + CuSO_4 + 2SO_2.$$
$$5.\ Cu_2O + 2SO_2 + 3O = 2CuSO_4.$$

The copper sulphate is decomposed as the temperature rises—

$$6.\ CuSO_4 = CuO + SO_3.$$

The sulphur trioxide set free in the equations 3, 5, and 6 reacts as follows:—

$$\begin{aligned} FeO + SO_3 &= FeSO_4. \\ FeS + 3SO_3 &= FeO + 4SO_2. \\ CuO + SO_3 &= CuSO_4. \\ Cu_2S + 3SO_3 &= Cu_2O + 4SO_2. \end{aligned}$$

$$\begin{aligned} 7.\ 2PbS + 7O &= PbO + PbSO_4 + SO_2. \\ 8.\ 3PbS + 10O &= 2PbO + PbSO_4 + 2SO_2. \end{aligned}$$

Lead sulphate is not decomposed by heat.

$$9\ \ 2ZnS + 7O = ZnO + ZnSO_4 + SO_2.$$

The zinc sulphate is only partly decomposed into zinc oxide and a basic sulphate at the temperature of lead ore roasting.

If silver sulphide is present in the ore it is decomposed, metallic silver and sulphur dioxide being formed.

The finely divided metal is then converted into silver sulphate by the free SO_3. It will, however, usually be found in the roasted ore as silver sulphate, undecomposed sulphide, and metallic silver.

If arsenic and antimony are present in the ore as sulpharsenides or sulphantimonides, part of the arsenic and antimony will be volatilized as sulphides, which become oxidized to As_4O_6, Sb_4O_6, and SO_2, part will be oxidized to As_2O_5 and Sb_2O_5, which will remain in the roasted product.

If they are present as simple sulphides, a larger portion will remain in the ore as stable antimonates and arsenates.

The operation of roasting is always more or less imperfect in practice, so that roasted lead ores all contain varying amounts of sulphates as well as unoxidized sulphides.

Pure argentiferous galenas are not treated separately in blast-furnace smelting, but are usually mixed with poor ores.

Roasting Furnaces.—The roasting of lead ores is rarely practised alone in heaps, and never on a large scale in stalls or kilns. Heap roasting is only employed where the ores are very pyritic, poor in lead, with much pyrites or zinc blende, and then usually in conjunction with a reverberatory roasting plant.

The heaps are constructed in the same way as for the roasting of copper ores. At Port Pirie, N.S.W., heap roasting is carried on, on a very large scale, for the roasting and sintering of slime, about 100,000 tons being treated annually. The slime is dried, cut into blocks, and the blocks are built into heaps, with big channels along the bottom, the sides being plastered with slime. Each heap is 200 to 250 feet long, 20 to 22 feet wide, and 6½ feet high. The sulphur is reduced from 12·5 to about 7 per cent.

Reverberatory furnaces of various kinds are or have been employed, the ores being for the most part in a fine condition when received at the smelting works, but since the introduction of the Huntington-Heberlein and other "blast" roasting processes, they have been more or less given up at many of the largest smelters.

The most important of these furnaces will now be considered.

The Long-bedded Hand-worked Roaster.—Only a few of these hand-worked furnaces survive in America. It is described on pp. 23-25. In some cases, it is made with a bed only 40 feet long and 14 feet wide, but a longer bed, 70 to 80 feet, is generally preferred. As a roaster for fine lead ores containing, say, 25 per cent. lead, it is said to give better results than any mechanical furnace. It is worked in the same way as for copper ores, the charge being exposed to a gradually increasing temperature by transferring it from hearth to hearth with frequent rabbling until it reaches the fire-bridge end of the furnace. Greater care is required to avoid clotting than in roasting copper ores. The ore, after being roasted in this furnace, is in the form of more or less coarse or fine powder, and in order to obtain it in an agglomerated form, suitable for the blast furnace, a special hearth, called a "fuse-box," was added in Colorado some years ago, in which the ore was fused. This "fuse-box" was, however, given up, owing to the great loss of lead and silver incurred by volatilization, and in its place a "sintering" hearth for merely agglomerating the ore, and not fusing it, was substituted.

The sintering hearth was the full width of the furnace, and adjoined the fire-bridge, which was low. The temperature was kept low, but sufficiently high to soften the ore, so that it would agglomerate. When drawn from the furnace it was usually beaten down into slag pots with a heavy iron disc, when it became quite compact.

The following details of a roasting and sintering furnace are given by Hofman.* The roasting part of the hearth is level without steps.

The main dimensions are—Roasting hearth, 74 feet by 14 feet; sintering hearth, 10 feet 4 inches by 14 feet; grate, 9 feet 9 inches by 1 foot 6 inches; height of fire-bridge above grate, 11 inches; above sintering hearth, 11 inches; height of step separating sintering and roasting hearths, 8 inches.

This furnace puts through in twenty-four hours 12 tons of a pyritic ore, poor in lead, and containing 28 to 44 per cent. sulphur.

Automatic Reverberatory Furnaces, sometimes called mechanical furnaces. —Several kinds are employed, and although they are extremely successful for roasting copper ores, they have a rather serious disadvantage when used for lead ores, in that the rabbling or turning over of the ore is uniform from one end of the furnace to the other, owing to the uniform speed of the rakes, whereas lead ores usually require to be more frequently turned over as they approach the hottest parts of the furnace. They have been given up at many works since the introduction of blast-roasting.

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* Hofman, *Lead*, p. 170.

The Brown Furnace (see p. 25).—It, or its modification, the Brown-O'Hara furnace, is or was in use in several of the leading smelting works; as, for example, the Globe plant at Denver, the Pueblo plant, Pueblo (Colorado), the Murray smelter, Utah, etc.

At the Globe smelter a Brown-O'Hara furnace, with hearth 90 feet long, roasts 26 tons of ore in twenty-four hours down to 3 or 4 per cent. sulphur.

The Ropp Straight-Line Furnace (see p. 29).—This is also an excellent furnace, but has not yet been employed to any great extent for lead ores. At the Selby Smelting Works a furnace, 105 feet by 11 feet, roasts 21 to 31 tons in twenty-four hours.

At the Hanauer Works (Salt Lake City) a large furnace, 180 feet by 16 feet, roasted 35 tons of leady ores containing 25 to 30 per cent. sulphur down to 5 per cent. in twenty-four hours.

These furnaces are also in use at Port Pirie for roasting lead concentrate (1906).

The Pearce Turret Furnace.—It was in use at two works in Pueblo (Colorado), but lead smelters who have had experience with it are not all quite satisfied with its work.

Brückner Cylinder.—A common size is 22 feet by 8 feet 6 inches. Capacity, 8½ tons of pyritic lead ores, containing 20 per cent. lead down to about 3 per cent. sulphur in twenty-four hours.

The chief disadvantages of this furnace are the production of much flue dust, and the difficulty of keeping the temperature low to prevent clotting in ores containing rather a high percentage of lead, and so it is no longer in use.

Revolving Cylindrical Furnaces with continuous discharge have not come into use for roasting lead ores, on account of the difficulty of keeping the temperature under control.

From the preceding considerations of the chief types of roasting furnaces, it may be said that for the general run of lead ores the hand-worked long reverberatory furnace was difficult to beat, although, on account of the cost of labour, the use of mechanical furnaces was until recently extending rapidly in large lead-smelting works. A radical change, however, in the methods of roasting and preparing the ore for the blast furnace has been brought about by the introduction of the "blast" roasting or "pot" roasting processes.

"Blast" Roasting or "Pot" Roasting Processes.—One or other of these processes, by reason of their efficiency and economy, has successfully replaced the old roasting furnaces at all the chief works. It is claimed for all that there is less loss of lead and silver than by the old methods of roasting.

There are two distinct types of apparatus and furnaces employed—namely, the "Up-draught" and the "Down-draught" type—yet both have much in common. The "Up-draught" appliances and processes are chiefly the following:—

1. The Huntington-Heberlein.
2. The Savelsberg.
3. The Carmichael-Bradford.

"The Down-draught" :—

1. The Dwight-Lloyd.

The Huntington-Heberlein and the Dwight-Lloyd processes are in extensive use in American works.

The sintering charge for both processes must not contain more than 16 to 18 per cent. of sulphur. When the ores contain larger percentages they must either be partly desulphurized by a preliminary roast, or must be mixed with material low or free from sulphur to bring the sulphur in the charge to be sintered down to the above proportions. Both these methods are sometimes followed in the same works.

Thorough mixing of the ingredients of a charge, in order to isolate the particles of sulphide as much as possible by other particles of more refractory material, is necessary for the most successful operation of all the processes.

The partial roasting is effected generally in Godfrey furnaces (see p. 39) or the Heberlein modification (see p. 39), also recently in Wedge furnaces (p. 36).

The Dwight-Lloyd machine has also quite lately been used as a preliminary roaster at East Helena, Montana, and for some time at Port Pirie. At the latter works one battery of Dwight-Lloyd machines is used for preroasting and another for final sintering. Both these objects cannot be attained in a single operation.

At East Helena the ore, after pre-roasting on a Dwight-Lloyd machine, is crushed, mixed with limestone, and finally blast-roasted in a Huntington-Heberlein pot.

In the *Huntington-Heberlein process*, the sulphide ore is first mixed with limestone, and also with siliceous flux and iron ore, if the ore does not already contain them in the proper proportions.

The mixture is then partially roasted. The roasted product, after being moistened with water, is charged into a large iron pot. Air is introduced at the bottom of the pot, and blown through the charge.

An exothermic reaction takes place, SO_2 and SO_3 are given off, the charge is agglomerated, and the sulphur contents reduced to about 3 or 5 per cent. The pot is then inverted and the charge dumped out. The mass is broken up into suitable sizes for the blast furnace. The charge should contain from 7 to 9 per cent. lime.

The preliminary roasting, which may be carried out in any ordinary roasting furnace, should reduce the sulphur to about 10 to 12 per cent. or lower. The pots, of which one is shown in Fig. 65, range in size from 9 feet in diameter and 4 feet 5 inches in depth, taking a charge of 8 tons, to 11 feet in diameter and 6 feet in depth, taking a charge of 12 to 15 tons.

A little above the bottom of the pot is a false bottom or grate, consisting of a perforated iron plate, below which is the opening for the admission of the blast. The pot is fitted with trunnions, so that it may be inverted, and during working is covered with a conical hood for carrying off the fumes.

The working of a charge is started by making a small wood or coal fire on the perforated plate, covering it with some hot roasted ore, and then charging in the partially roasted mixture of ores and fluxes. The charge is introduced generally in successive layers.

At the beginning a low blast is used, about 2 ozs.; in some works 10 ozs., and is gradually increased as the ore is filled in to from 10 to 15 ozs., or sometimes up to 20 to 25 ozs.

As it is important that the air should pass up evenly through the charge, it is pierced from time to time with an iron rod, and any large blowholes which may form are at once closed up. When the operation is finished, the top of the charge will be quite red hot and the ore agglomerated. The hood is then raised and the pot inverted, when, if the operation has been successful, the charge will fall out as a partially fused solid mass.

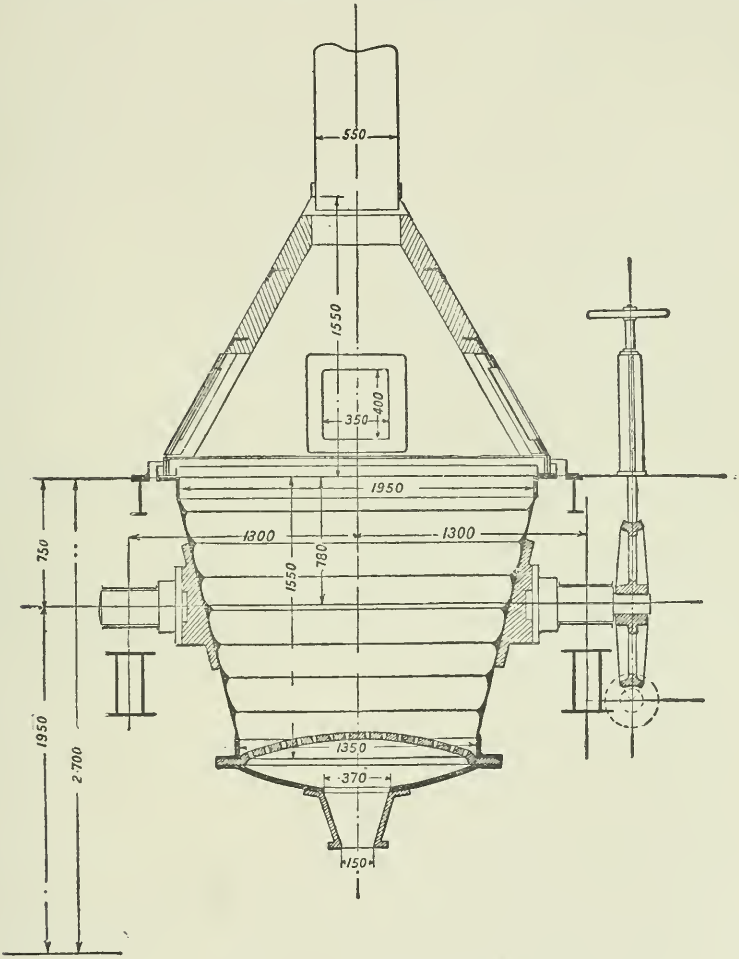

Fig. 65.—8-ton Roasting Pot.*

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* Collins, *op. cit.*, p. 114.

The time required varies in different works, according to the nature of the ores, from four to ten hours. The procedure and pressure of the blast also differ considerably.

At the Garfield Works of the American Smelting and Refining Company the process is carried on as follows:—The pots are of the Huntington-Heberlein type, each of which works off a charge of 8 tons in eight hours. The concentrate is first roasted down to about 12 to 17 per cent. of sulphur in MacDougall furnaces. After well mixing and moistening with 8 per cent. of water in a special pot, they are taken in that pot by a travelling crane and dumped into the pot to be blown, in which there is already a small charge of 1 ton of hot calcines. The blast, which is gentle at first, is gradually increased to 25 ozs., and then somewhat diminished towards the end of the blow. The sulphur is reduced to 6 per cent. The pot containing the sintered cake is carried by the crane to the breaking floor, where the cake is dumped out and broken up.

The Savelsberg process differs from the Huntington-Heberlein process in that the preliminary roasting is omitted, but enough limestone and siliceous flux must be present to form a proper slag. The mixed ore and fluxes, after being moistened, are charged direct into the sintering pot, and the operation is carried on as described under the Huntington-Heberlein process.

The pots, too, resemble those of that process, but each is supported by trunnions on a truck.

At the St. Joseph Lead Company's plant, Flat River (Mo.), the blast is 10 ozs. at the commencement, and gradually rises to 20 or 25 ozs. at the finish, the time of the operation being about ten hours for a charge of 10 tons. Dwight-Lloyd machines have now been installed at this plant.

The Carmichael-Bradford process differs from the two preceding processes in that the ore is mixed with gypsum instead of limestone. The ore is not roasted, but the gypsum has to be first partially calcined. The process has only been put into practical use at Broken Hill, where gypsum is available at a low cost. The time of the operation there is about three hours.

The up-draught methods of blast roasting are accompanied by the following disadvantages:—

1. The process is intermittent.
2. Much labour is required in charging, working the charge, discharging and breaking up the resulting mass.
3. The ore is unevenly roasted and sintered.
4. The loss of lead is liable to be great, owing to the length of time the charge is exposed to a high temperature.

Down-Draught Roasting and Sintering Process.—In order to more or less overcome the above-mentioned disadvantages the following apparatus and process has been devised by Dwight and Lloyd, and bears their names.

The Dwight-Lloyd apparatus is of three types—the straight-line machine, the horizontal table machine, and the drum machine.

*The Straight-Line Machine.**—This machine has been selected for most of the recent installations.

Its construction is shown in Fig. 66. The ore is fed upon a travelling grate in the form of an endless conveyor made of small truck-like elements,

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* Hofman, International Congress of Chemistry, 1909. Report in *Min. Mag.*, vol. iii., pp. 146, 147.

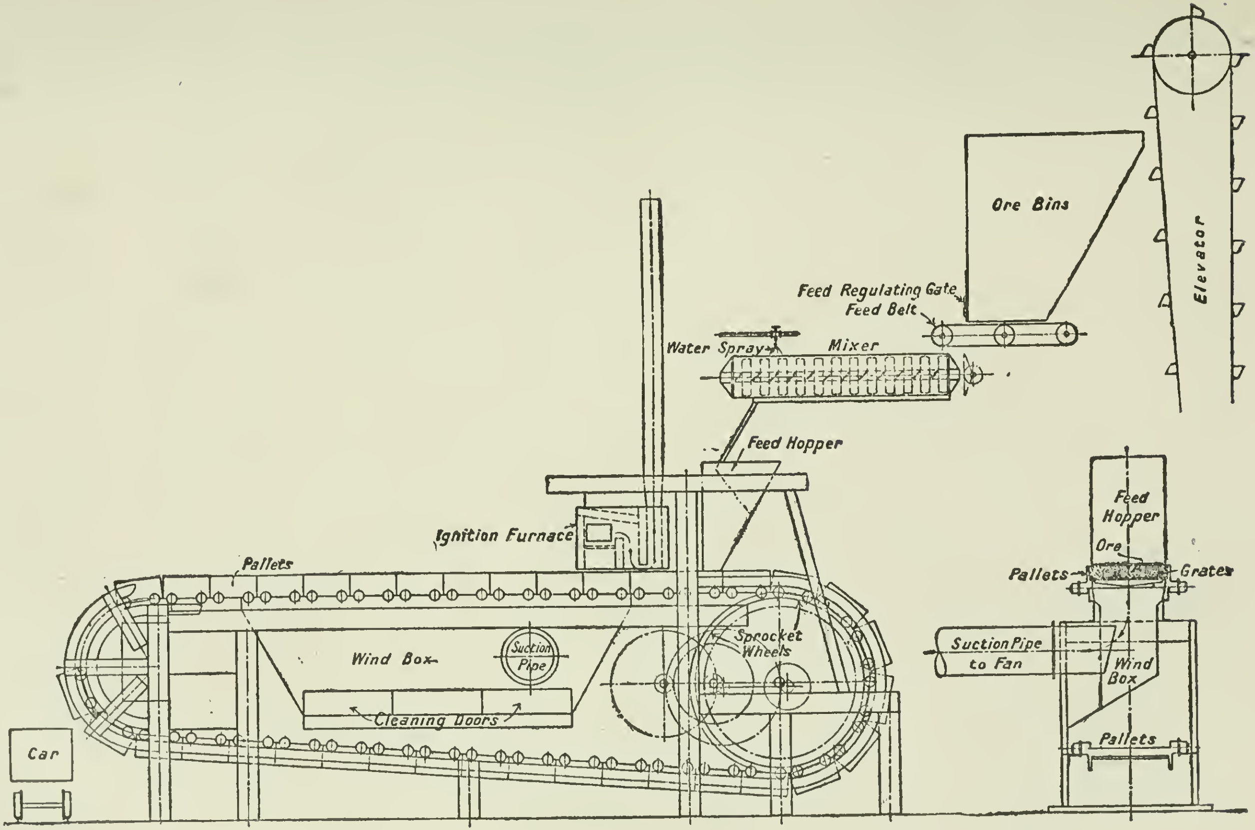
Elevator
Ore Bins
Feed Regulating Gate
Feed Belt
Water Spray
Mixer
Feed Hopper
Ignition Furnace
Pallets
Wind Box
Suction Pipe
Cleaning Doors
Sprocket Wheels
Car
Feed Hopper
Ore
Pallets
Grates
Suction Pipe to Fan
Wind Box
Pallets

Fig. 66.—Dwight-Lloyd Straight-Line Sintering Machine. (Levy, *Modern Copper Smelting*, p. 60).

called "pallets," all independent of one another, each of them having four wheels running on guide rails. While passing over the suction-box the pallets glide along the top of the sides of the box on their planed bottoms instead of on the rails, and at each end of the suction-box a planed plate is provided on the track for the pallets to glide over, thus preventing any leakage of air. The little wheels engage in the teeth of sprocket wheels to the right, and these push the train of pallets along. At the discharge end, to the left of the drawing, the guide rails raise the pallets slightly so as to dislodge the cake of sinter from the grate slots. On passing round the circular guides each pallet falls against the preceding one, and the concussion throws the cake into the car. The return journey is made by gravity along the inclined guides at the bottom. The igniter is a small furnace burning coal and built of tiles. The flame, after passing over the fire-bridge, is deflected downward upon the ore by an adjustable brick hood. The machines vary in size. That at the Ohio and Colorado Smelting Company's Works, Salida, measures 30 feet long over all, and the suction-box 13 feet by 2 feet 6 inches. The distance between the brick hood and the surface of the ore is 2 inches; the rate of travel is 8 inches per minute; the vacuum in the suction-chamber is 6 ozs. The charge is a low-grade mixture, containing 17½ per cent. sulphur and 35 per cent. silica; the discharged sinter contains 4 per cent. sulphur; and the capacity is 50 tons per twenty-four hours.

The straight-line machine with pallets 12 inches wide and an effective hearth area of 42 by 264 inches (77 square feet) is the type which has been installed in most new plants. Its capacity is rated at 100 tons per day, but at some works a much larger quantity is treated.

As regards the size of the particles, it is found that none should be greater than ¼ inch, and that not more than 25 per cent. should be as large as this. It is necessary that the constituents of the charge should be intimately mixed and uniformly moistened with from 6 to 10 per cent. of water.

The Drum Machine.—This consists of a slowly revolving drum carrying a series of cast-iron perforated grates. Inside the drum, and occupying about one-fourth of its upper portion, is a fixed suction-box. The ore previously wetted is fed from a hopper to form a layer on the grates, usually 2 to 4 inches in thickness, and as the drum revolves is passed under the flames of a series of gas or oil burners. Its upper surface is ignited, and as it travels over the suction-box the roasting of the entire layer is completed. The discharge of the roasted ore is effected by the points of an upturned grating, which are fixed close to the surface of the perforated grates.

The Horizontal Table Machine.—This is a horizontal circular revolving table, with an outer diameter of 15 feet and an inner of 8 feet, and having for its top a series of perforated grates. The suction-box is fixed below, and the ignition furnace, or gas, or oil jets above. The sintered ore is removed by means of a scraper.

In all the above machines, when the operations have been carefully performed, the roasted and sintered ore will be obtained in porous and coherent masses suitable for the blast furnace.

The Dwight-Lloyd machines have been installed in several works as at the St. Joseph Lead Company's Smelter (Mo.), where they have displaced the Savelsberg process; at the Broken Hill Smeltery at Port Pirie, where they have displaced the Carmichael-Bradford process; at Trail, B.C., two 100-ton machines, and at other places.

As regards the reactions that occur in blast roasting, many theories, more or less elaborate, have been advanced, but, in a recent thesis by Paul Richter, it is held that they are nothing more or less than those of an enforced ordinary roast, such as that in a reverberatory furnace.

An experimental investigation of the reactions has been made by C. O. Bannister,* the results of which he summarizes as follows:—

(*a*) The oxidation of lead sulphide takes place in three stages—(1) its partial oxidation to a mixture of sulphate and oxide; (2) a reaction between sulphide and sulphate; and (3) a reaction between sulphide and oxide.

(*b*) In the presence of lime, limestone, or magnesia, the sulphates of calcium or magnesium are formed in preference to sulphate of lead, leaving a much larger quantity of lead in the roasted material as oxide.

(*c*) Silica and calcium sulphate act merely as diluents, taking no chemical part in the reactions until a temperature of over 1,000° is reached.

(*d*) Ferric oxide in certain physical states appears to act as a catalyzing agent, lowering the temperature of oxidation of lead sulphide, and increasing the amount of lead sulphate formed during the roast.

(*e*) Silica acts at high temperatures, 1,000° and above, in decomposing lead sulphate and calcium sulphate, the latter being thus decomposed, whether it is added as such or formed during the preliminary stages of the roast.

Professor Hofman, however, whilst acknowledging the value of the results of these experiments as regards a draught-roast of long duration at a low temperature, does not think that they can be applied directly to the explanation of the reactions that take place in a blast-roast at a high temperature. Hence, it would seem that further research is still needed before we can say with absolute accuracy what are the reactions which occur in the blast roasting of galena.

The following are the chief advantages which are claimed for the blast-roasting processes:—

1. The ore is sintered with a low sulphur content, and is obtained in a most suitable form for the blast furnace.
2. The SO_2 given off can be utilized for the manufacture of sulphuric acid.
3. The workmen suffer very little from lead poisoning.
4. The time of actual smelting in the blast furnace is lessened, hence the output is increased.
5. Less loss from flue dust.
6. The total costs of smelting the ore are diminished

Blast Furnaces.—Modern furnaces are always water-jacketed at the boshes and tuyere zone.

There are two chief types:—

(*a*) The circular furnace, which is generally employed in Europe, and only in small works elsewhere.

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* *Trans. Inst. Min. and Met.*, vol. xxi., pp. 346, *et seq.*

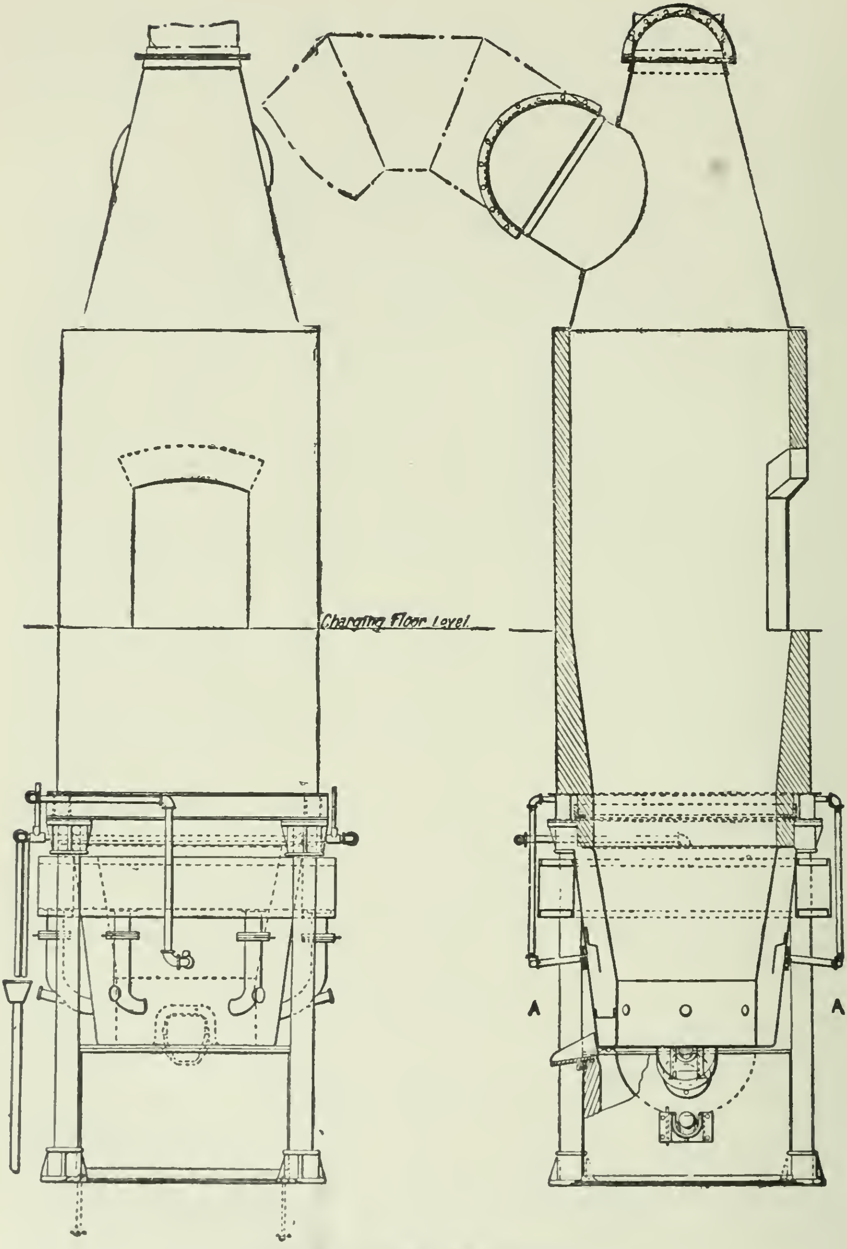
Charging Floor Level
A
A

Fig. 67.—Circular Blast Furnace.*

* From Drawing supplied by Messrs. Fraser & Chalmers.

(*b*) The rectangular or oblong furnace, which is in practically universal use in America and in other countries where large quantities of ore have to be treated.

Circular Furnaces.—The great disadvantage of the circular furnaces, as has been pointed out under copper furnaces (p. 95), is that their diameter cannot be increased beyond 60 inches, and is best somewhat less, say 42 or 48 inches, as beyond this the blast can only penetrate with difficulty. The output is, therefore, limited, and hence their use is confined to small plants and for smelting residues. The output will vary with the nature of the ore and fuel, a furnace 36 inches in diameter at the tuyeres may, however, be expected to smelt 25 to 50 tons of ore in twenty-four hours.*

One of the best forms of circular furnaces is shown in Fig. 67. The illustration requires but little explanation. The shaft which is supported by a cast-iron mantle plate, which rests on four cast-iron columns, is built of fire-bricks, and is cased with iron plates. The boshes consist of water-jackets, which extend to the top of the crucible or lead well, and carry the tuyeres.

The crucible is built of fire-bricks firmly braced together with steel plates. The lead is removed from the crucible by means of an Arents' automatic tap (see p. 205). The tuyeres are connected with the blast main by iron pipes.

Rectangular Furnaces.—They vary greatly in size, and except for oxidized ores the smallest size that is popular among lead smelters is 120 inches by 42 inches at the tuyeres, although the size 42 inches by 84 inches may do good work.

In the following table the dimensions, etc., are given of the furnaces in use at several important works :—

TYPICAL BLAST FURNACES.

	Dimensions at Tuyeres.	Blast Pressure.	Smelting Column.	Capacity.	Remarks.
		Ozs.	Height.	24 hours. Tons.	
United States Smelting and Refining Co., Utah, . . .	45″×160″	..	16′ to 18′	200	Mech. feed.
Tintic Smelter, Silver City, . . .	48″×160″	32 to 34	..	..	Coke, 12 %
American Smelting and Refining Co., Pueblo, Colorado, . .	48″×148″	34	..	150	Mech. feed.
Globe Plant, Denver, .	42″×144″	32	18′	120 to 150	..
Murray Plant, Utah, .	48″×164″	34	20′	166	Coke, 12 %
Port Pirie, Australia, .	62″×212″	30	21′	150	..
Perth Amboy, New Jersey, . . .	44″×128″	35	16′	140	Coke, 12 %
Laurium, Greece, 1908,	48″×160″	35 to 40	20′	250 to 275	Coke, 14 %
Northport, Wash., .	42″×192″	30 to 40	18′	250	Coke, 12 to 13 %

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* An exception to this statement is a circular lead-smelting furnace at Pertusola, Italy, built by Mr. Thomas Huntington in the late eighties. It is 2·42 metres in diameter at the tuyeres, and is supplied with a double row of tuyeres 42 mm. in diameter. At present (1918) it is smelting rather over 200 tons of smelting mixture per 24 hours at a blast pressure of about 30 oz.

A general view of a rectangular furnace is given in Fig. 68.

Two of the most important measurements of a blast furnace are :—

1. Breadth at the tuyeres. This for several ores will range from 36 to 44 inches or 48 inches.

2. Depth of the tuyeres below the upper surface of the charge, the working column. If too little, the furnace will work with a hot top, and there will be great volatilization of lead. During recent years it has been increased from 12 or 14 feet to 20 feet. " The increase in height has been necessitated by the greater pressure of blast required for the highly siliceous and calcareous slags" (*Hofman*).

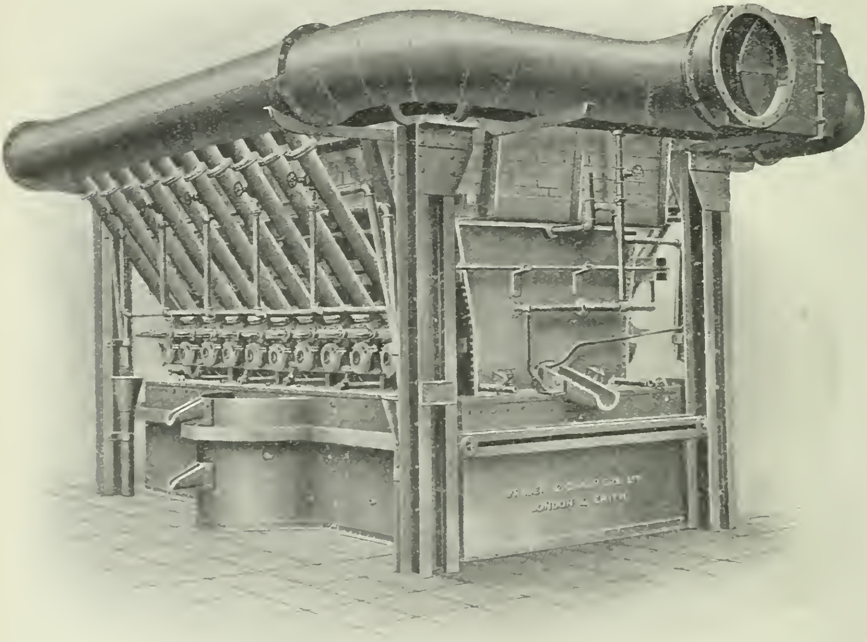


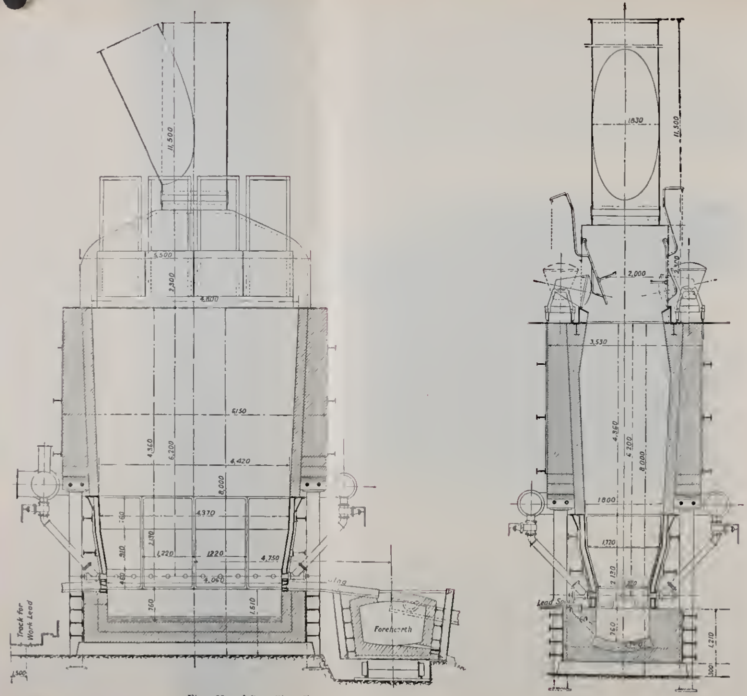
Fig. 68.—Rectangular Blast Furnace for Lead *—General View.

3. The height of the tuyeres above the level of the lead in the hearth is also important; it should be just sufficient to keep the metal well molten. It is about 10 to 12 inches in many furnaces.

The foundation is best on rock, but this is not always available, and usually an excavation has to be made to a greater or less depth before suitable ground is met with.

A thick bed of concrete should then be put in, or if there is a furnace at work, the excavation should be partly filled with molten slag. Above either

* Messrs. Fraser & Chalmers.


11,500
5,500
2,300
4,800
6150
4,360
6,200
4,420
8,000
4370
60
910
2,130
1,220
1220
4,750
460
4,060
Slag
760
1,610
Track for Work Lead
500
Forehearth
1830
11,500
2,000
2,300
3,530
4,360
4,200
8,000
1800
1,720
2,130
720
Lead Spout
760
1,210
300

Figs. 69 and 70.—Blast Furnace* (Laurium). (Collins, *Lead*, Figs. 97 and 96).

of these, brickwork reaching to the ground level should be laid. This should extend to at least 3 feet beyond the bed plate and the four columns. A wrought-iron or steel bed plate is then carefully bedded on top of the brickwork and clear from the columns. This prevents any lead which may leak out of the hearth passing into the ground.

In Figs. 69 and 70* is shown a typical furnace. The shaft is supported on cast-iron columns, as usual, so that the lower part of the furnace can be taken down without affecting it. It is best built of fire-brick, but the outside is often of common red brick. Brick shafts are now, however, being given up (see next page). It rests on four cast-iron plates supported by wrought-iron or steel girders, which pass from column to column. It is braced with wrought-iron tie-rods, I beams, and cast-iron corner pieces. At the feed-floor there are usually two counter-balanced charging doors on each side. In the furnace at Laurium, as shown in the figures, there are four doors on each side, which open automatically. The top of the furnace is closed usually by a fire-brick or iron hood, with an opening at the top for a short stack, which is closed by a damper, and one at the side for the downcomer, by which the fume passes to the flue leading to the chimney stack. The downcomer, which is generally of iron lined with fire-brick, rises at an angle of 45° for a short distance before descending to the flue, and is about 4 feet 6 inches to 5 feet in diameter.

Hoods extending above the charging floor and carrying the downtake are now being adopted generally as the discharge of the gases by a downtake below the charging floor, found in some of the older plants, necessitates too high a drop for the charge, and gives rise to irregular working of the furnace, and the escape of much dust. End doors are provided for the admission of the charge cars, and side doors for barring down or feeding by hand when necessary.

The bottom of the hearth is an inverted arch of fire-brick, not resting directly on the bed plate, but on a layer of a mixture of raw clay and ground bricks firmly beaten down. The side walls are also of fire-brick, sometimes tapering. They should not touch the iron plates that enclose the hearth, but a space of 2 inches should be left, which is filled with the above mixture, or with raw clay mixed with ground coke. The side plates of the hearth are of stout boiler plate firmly bound together with old rails or I beams, with their ends braced with heavy clamps or held by tie-rods. In some cases they are ribbed castings bolted together. The hearth has an Arents' automatic tap, which consists of a channel about 6 to 8 inches square, leading from the lowest part of the hearth to its top outside the furnace, where it is expanded into a basin. It is usually placed in the middle of one of the long sides of the hearth. In the largest furnaces there are sometimes two.

The construction of the hearth or crucible of the furnace at Laurium is shown in Fig. 71. The magnesia bricks are made of a mixture of 3 parts of calcined magnesite and 1 of chromite, and are burnt at a very high temperature.

When the furnace is working the hearth is always full of lead, which, rising in the channel, fills the basin, and either flows from it into a cast-iron pot placed in front or in small works is laded direct into iron moulds. The moulds are white-washed, to prevent the lead sticking and hold about 120 lbs. each.

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* Collins. *op. cit.*, p. 182.

If the ores contain much copper the Arents tap must be made larger, even 12 inches square, so that the pasty masses of cupriferous lead alloy, which are liable to accumulate at the bottom of the crucible and close the channel, may be removed. A taphole is provided at the bottom of the hearth opposite the bottom of each Arents' tap for emptying the furnace when necessary. The water-jackets are placed on the top of the walls of the hearth, and form the boshes and the sides of the tuyere zone. They range in height, according to the size of the furnace, from about 3 feet 6 inches to about 6 feet or more. For details of their construction and the supply of water for cooling them, see Copper, pp. 103-104.

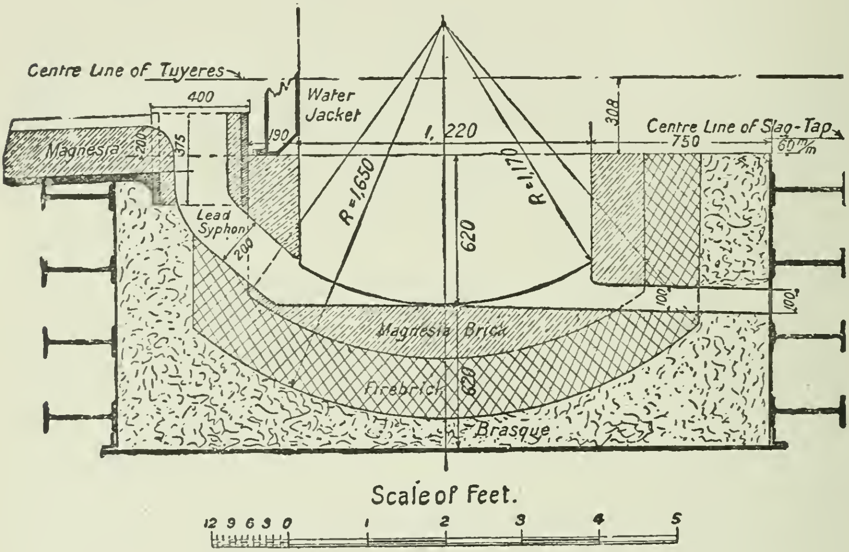
Centre Line of Tuyeres
400
Water Jacket
190
220
308
Centre Line of Slag-Tap
750
60 m/m
Magnesia
200
375
Lead Syphon
200
R=1,650
620
R=1,170
100
100
Magnesia Brick
Firebrick
620
Brasque
Scale of Feet.
12 9 6 3 0
1
2
3
4
5

Fig. 71.—Crucible of Blast Furnace * (Laurium).

All new blast furnaces have two tiers of water-jackets reaching from the top of the crucible up to the charging floor or a little below it.

An important modification of a lead blast-furnace top is shown in Fig. 71*a*,† representing one of the blast furnaces at El Paso.

It consists of a box or hood closed at the top and at one end, but open to the downtake flue at the other end, and also open below. Cast-iron plates of suitable form, built into the brick shaft of the furnace, support it, so that the lower narrow end is 6 ft. 6½ inches below the top. The hood is tapered toward the bottom, to correspond with the batter of the shaft-wall, maintaining a space 2 feet wide on each side lengthwise the furnace. The charge-car is seen centered over the plate covering the top of one wall. The door on

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* Collins, *op. cit.*, p. 184.

† Courtenay de Kalb, *Mining and Scientific Press*, May, 1918, pp. 681 and 684.

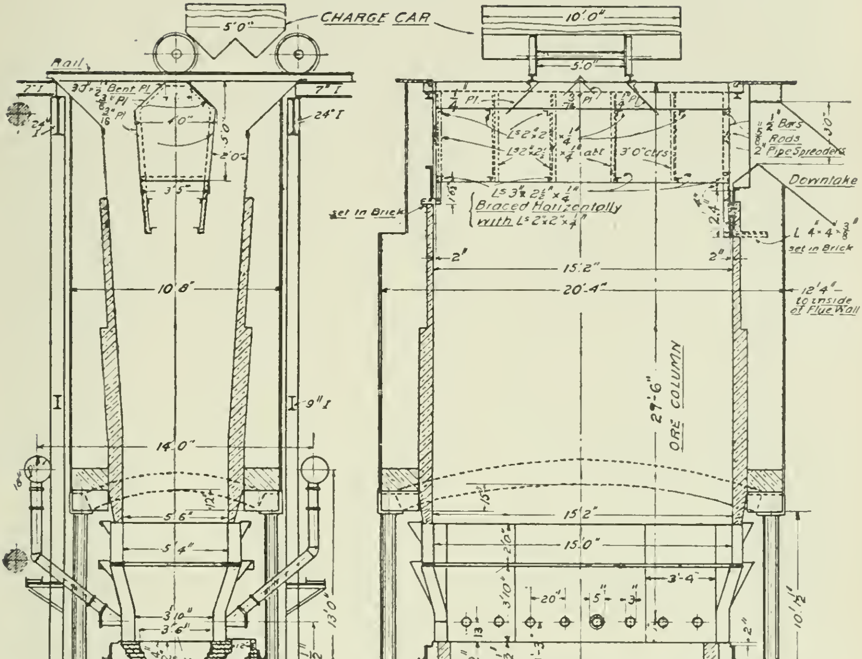
CHARGE CAR
5'0"
10'0"
Rail
7"I
24"I
4'0"
5'0"
2'0"
3'5"
10'8"
9"I
14'0"
5'6"
5'4"
3'10"
3'6"
13'0"
5'3½"
set in Brick
Braced Horizontally with Ls 2"×2"×¼"
½" Bars
Rods
2" Pipe Spreaders
Downtake
L 4"×4"×⅜" set in Brick
2"
15'2"
20'4"
12'4" to inside of Flue Wall
27'6"
ORE COLUMN
15'0"
3'4"
20"
5"
3"
10'1½"
CROSS SECTION
LONGITUDINAL SECTION
25'0"
Downtake
10"×10" Holes
L 4×4×⅜
13'6"
TOP VIEW
15"
19'4"
12'0"
9'8"
11"
12'9½"
4'3"
CRUCIBLE
17½
7'2"
16"
12"
2'4"

Fig. 71*a*.—Lead Blast Furnace, El Paso Smelting Works, Texas.

the left side is dropped and, as the charge dumps, the coarser pieces gravitate towards the hood. Thus the greater part of the fine material remains on the outside next to the shaft-wall, while the coarser ore accumulates at the centre, leaving the charge more permeable by the gases directly underneath, and the fume naturally follows this line of least resistance into the hood and thence to the flue. Doors are provided in the top of the hood in order to observe the condition of the charge and to gauge the heat of the furnace. The beneficial results are numerous and important. In the first place no fume escapes from the top of the charge at any time if the proper burden is maintained. The concentration of the heat in the centre of the furnace tends to reduce the formation of wall-accretions, and the fine ore being kept toward the outside is not in the path of the greater movement of gases. This has an important effect in curtailing the dust loss. Moreover, it is found that the coke-consumption is materially less than with furnaces operated alongside, that treat identical ore-mixtures, but are unprovided with the hood. This and similar furnace tops are termed "thimble" tops.

Water-Jackets.—With the higher charge columns and blast furnaces of modern practice the smelting zone extends further upward than formerly, hence, as I have already stated, most new blast furnaces have two tiers of water-jackets reaching from the top of the crucible up to or just below the charging floor.

Water-jackets are constructed of mild steel plate, sometimes of cast-iron, but those of the former material have two great advantages over those of the latter, they have a much longer life and do not crack.

"The water of the jackets is kept at about 70° C., the usual test being that the hand can be quickly passed through the outflowing water without being scalded. Any irregularity in the temperature of the jackets indicates that the coating on the inside is thicker on some than on others."* The water should not be fed into the jackets near the bottom but about the middle or near the top, and each jacket should have its own supply.

"It is true that a considerable amount of the heat developed in the furnace, perhaps 10 per cent., is carried away by the cooling water of the jackets; their advantages, however, are so great that in non-ferrous blast furnaces they have replaced everywhere firebrick and other refractory materials."†

Tuyeres.—The tuyere holes in the side jackets are about 10 or 12 inches from the bottom.

In most furnaces there are no tuyeres in the end jackets, but the last tuyeres in the sides are brought rather close to the ends. The tuyeres, in ordinary practice, range from about 3½ to 4 inches in diameter, and are connected with the bustle pipe by galvanized iron pipes, as shown in Fig. 69.

A very convenient form of tuyere, which has found much favour in Mexico, is the Robinson air-tight non-slagging tuyere, shown in Figs. 72 and 73.‡ This has a downward extension 4 inches in diameter, closed by a disc of fusible metal, which melts before the slag actually reaches it, and since the slag by this arrangement can pour out freely, neither the peephole nor the air inlet can ever become completely obstructed. Another advantage of this tuyere is that it is practically air-tight; at Mapimi the saving in blast resulting from the adoption of this tuyere is said to be nearly 20 per cent.

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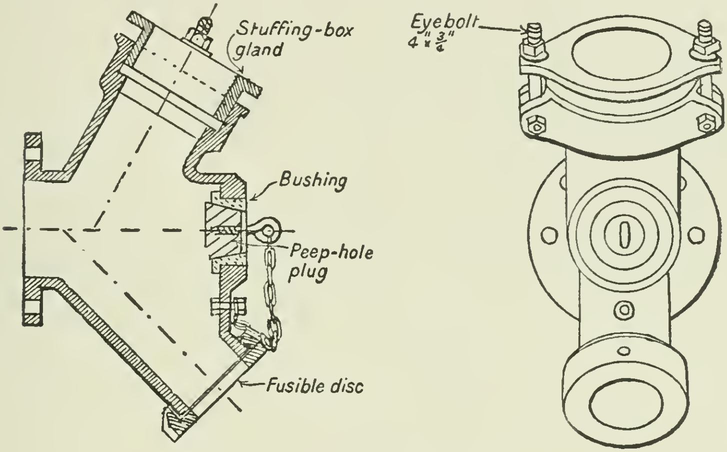
* Hofman, *Metallurgy of Lead*, p. 308.
† *Ibid.*, p. 235.
‡ Collins, *op. cit.*, p. 200.

The shaft furnaces for lead smelting at Monteponi, Sardinia, are of the American type, but the water-jackets have been replaced by walls of cast steel, 0·75 inch thick, which are cooled by external water sprays. It is claimed that the water consumption is considerably reduced by this system, while all danger of leakage from the jackets is eliminated.

The Blast.—This is furnished by rotary positive-pressure blowers, especially the Root or its modification, and is never heated. With the high pressures now in use cylinder blowing engines have been introduced, on account of the back leakage of rotary blowers, but in some works, as at the Garfield and Murray (Utah), rotary blowers have replaced them. It is best for each furnace to have its own blowers, but usually a blast main, into which all the blowers work, runs behind the row of furnaces, and the blast is led to each by a branch pipe.



Figs. 72 and 73.—Robinson Tuyere.

The pressure is measured by a mercury, water, or glycerine gauge (1 inch of mercury = about 14 inches water = about 11 inches glycerine = 8 ozs. avoir. pressure). Formerly the pressure of the blast rarely exceeded 20 ozs. per square inch, and was generally lower, but in modern furnaces it frequently reaches 40 to 50 ozs., or less frequently 60 ozs. This increase has been necessitated by the widening of the furnace in order to get a greater output, by the lengthening of the smelting column, and the less fusible character of the slags from the ores now frequently smelted.

Slag and Matte Outlet.—The matte, speise, and slag collect in the crucible above the lead. In large furnaces they are allowed to flow out continuously through an ordinary water-jacketed trapped spout into a forehearth or settler (Fig. 74), in which they are separated. In small furnaces they are tapped out as they accumulate. The outlet is usually in one of the ends of the furnace, but sometimes in both.

Charges.—At many large works where the ore from the mine is irregular in composition, or ores are received from several mines as at "custom" works, the so-called "bedding" system is followed, in order that the charges for the blast furnace and roasters may be tolerably uniform in composition, and thus regular working of the furnaces be ensured as far as possible.

The lots of ores as received, after sampling and arranging, are hence not dumped into separate bins, but are spread in layers to form a bed, in such a manner that its composition will approximate to a standard suitable for the work of the smelting plant, and from which the furnace charges are drawn.

This system, however, has been given up at most works, and the practice of storing the ores in separate bins, according to their composition, adopted; in this case, the charges for the furnaces are made up by taking definite weights of ore from each bin by means of cars, carrying a weighing apparatus, and by which they are transferred to the roasting furnaces; or to the blast furnaces, together with the necessary fluxes which have been similarly stored. Blast furnaces for smelting lead ores are generally hand-fed, but in some works, as at the Pueblo Smelting and Refining Company's plants, Pueblo (Colorado), and the works of the American Smelting, Refining and Mining Company, Utah, and others, mechanical feeding has been adopted with success.

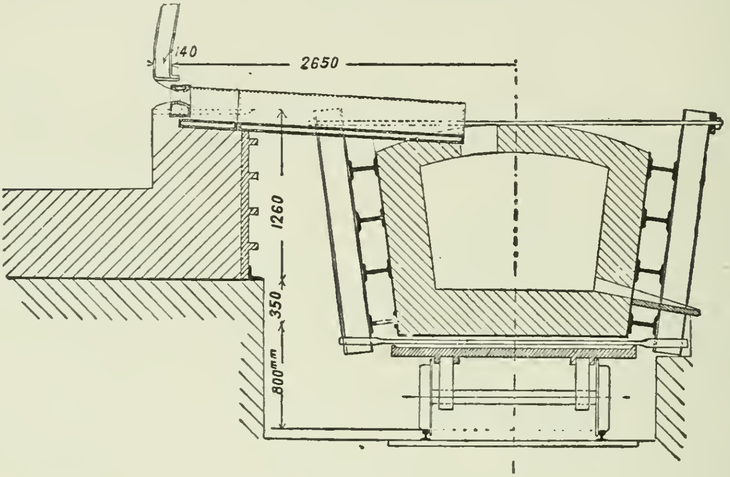


Fig. 74.—Forehearth * (Laurium).

Mechanical feeding is now being adopted in all new plants.

The ordinary arrangement of cup and cone is not suitable for rectangular furnaces. At Pueblo, three cast-iron deflectors of the shape of an inverted

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* Collins, *op. cit.*, p. 216.

V extend across the shaft about 18 inches above the stock line. The charge of about 5 tons is dumped from the bottom of a specially constructed car, and as it is dropped it is distributed by the deflectors.* See also p. 206.

The ore and fluxes are sometimes mixed, but the fuel is charged separately, and usually in alternate layers with the ore and fluxes. It should be kept somewhat more in the centre than the latter. The ore fines should be fed more to the sides than to the centre to cause the gases to ascend uniformly through the smelting column, otherwise the tendency will be for the gases to pass up at the walls, and the furnace will work irregularly.

When a furnace is working satisfactorily the charge will sink regularly, and the top of the smelting column will be cool.

The material charged into the furnace should have such a composition that it will yield a slag which is a monosilicate, $2RO, SiO_2$, or $2R_2O_3, 3SiO_2$. The former is the common lead blast-furnace slag, but sometimes the sesquisilicate is necessary.

In blast-furnace smelting it is a common practice to mix the roasted ores with suitable proportions of unroasted ores, rich argentiferous ores especially being added to the charge without previous roasting. It is not often that the ores will yield a proper slag when smelted alone, so that in order to obtain it fluxes are required. It is important to avoid the use of barren fluxes; therefore, ores containing lead, silver, or gold, suitable for giving a proper smelting charge, should be obtained whenever possible as the metals they contain will be recovered. The total amount of lead in the entire charge should be from 12 to 18 per cent., or upwards to 25 or 30 per cent., and should not be less than 8 per cent. As a rule, 10 per cent. is the minimum, as with less than this the silver is not satisfactorily collected in the base bullion. Richer ores are generally mixed with poor ores or with silver ores.

There must be sufficient lead to collect the silver in the ore, and the charge should be arranged so that the work-lead should not contain more than 300 ozs. silver per ton, although in the United States and Mexico it sometimes contains 500 ozs.

In Missouri, where a rich galena concentrate is smelted, the aim is to extract the lead primarily for its own sake, with a minimum of fluxes, only barren material being available; the charge is rich in lead up to as much as 45 per cent.

All that goes into the furnace—that is, ores, fluxes, fuel, and foul slags—should be weighed.

Fuel.—Either coke or charcoal, or a mixture of both, may be used as fuel, but coke where procurable at a moderate price is most frequently used. The amount required will range from 12 to 15 per cent. of the weight of the charge.

Fluxes.—The usual fluxes employed are the following:—

1. *Silica*, as siliceous silver ores, if they can be obtained, otherwise as quartz, or sandstone, for fluxing basic ferruginous or calcareous ores.

2. *Iron Ore.*—" This is a favourite flux for siliceous ores whenever obtainable, more especially because, when derived from the gozzans of ore deposits, it usually carries more or less silver and gold, and sometimes lead. Its cost alone precludes its more extensive use for simple fluxing purposes when not carrying any 'values.' "

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* *Eng. and Min. Journ.*, January, 1903, p. 114.

"It is impossible too strongly to impress upon the novice that in the ordinary lead blast furnace a deficiency of iron lies at the root of most of the difficulties and irregularities in furnace manipulation, except those caused by zinc, and that the troubles caused by an excess of base (especially of iron) are much less to be feared than those due to an excess of silica."

"A pretty safe rule for the inexperienced metallurgist to follow is 'when in doubt or in trouble increase the iron ore on the charge'" (*Collins*).*

Iron ore also acts as a reducing agent in the presence of carbon.

3. *Limestone*, or calcareous ores for fluxing silica, are widely used. They assist in producing a clean slag by expelling lead and copper oxides from their silicates. They also reduce the specific gravity of ferruginous slags.

One or more of the above materials will, as a rule, have to be added to the furnace charge.

For a monosilicate slag, $2RO \cdot SiO_2$.

100 parts of SiO_2 require 186 parts of CaO.
,, ,, ,, 240 ,, FeO.
,, ,, ,, 114 ,, Al_2O_3.

According to Eilers,† the requirements of a good slag are "that it should not contain over 0·75 per cent. lead, or ½ oz. of silver to the ton, provided that the base bullion does not run higher than 300 ozs. silver per ton, nor have a density over 3·6, nor permit accretions in the hearth, nor any creeping up of over-fire."

The slags in the following table have been thoroughly tested, and are in successful use (Hofman, *Metallurgy of Lead*, p. 276) :—

Authority.	SiO_2.	Fe(Mn)O.	Ca(Ba,Mg)O.	Total.
Eilers, . . .	28	50	12	90
,, . . .	30	40	20	90
Livingstone, . .	30	36	20	86
Iles, . . .	32	33	23	88
Schneider, . .	33	33	24	90
Page, . . .	33	36	16	85
Hahn, . . .	34	50	12	96
Raht, . . .	35	27	28	90
Hahn, . . .	36	40	20	96
Murray, . . .	40	34	26	100

The silica, iron oxide, and lime will be found to range as follows :—

SiO_2 from 28 to 40 per cent.
FeO ,, 27 to 50 ,,
CaO ,, 12 to 28 ,,

According to Iles (*Lead Smelting*, p. 90), no attention need be paid to zinc in slags until it runs over 6 per cent.

In selecting one or other of these slags, it is important to consider not only the metallurgical conditions necessary for giving the best slag, but also and chiefly the economic conditions which are suitable for smelting the ore so as to yield the greatest profit. The latter will generally depend on the fluxes or ores which occur in the locality or its neighbourhood.

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* Collins, *op. cit.*, p. 131.

† *Eng. and Min. Journ.*, April, 1891.

Reactions in the Blast Furnace.—The following are the principal reactions which occur in smelting lead ores in the blast furnace :—

(*a*) $2PbO + C = 2Pb + CO_2$.
(*b*) $PbO + CO = Pb + CO_2$.
(*c*) $Fe_2O_3 + CO = 2FeO + CO_2$.
(*d*) $FeO + C = Fe + CO$.
(*e*) $PbS + Fe = Pb + FeS$.

Some lead is always reduced above the smelting zone by the reactions between PbS and PbO and $PbSO_4$ (p. 177).

As the charge descends, any PbO is reduced by carbon in the upper zone, as in (*a*). At a bright red heat lower down in the smelting column it is reduced by CO, as in (*b*). Fe_2O_3 is first reduced to FeO by CO, as in (*c*), part of which combines with SiO_2 to form slag, and part is decomposed by the action of C, and Fe is set free in the smelting zone, as in (*d*). This Fe then acts on the galena (PbS), liberating Pb, as in (*e*).

All these reactions are complete about half-way down the smelting column. As the reduced lead trickles through the charge in the smelting zone, it collects any gold or silver which may be present and passes into the well.

Lead silicates are not decomposed by C or CO, but at a high temperature FeO, also CaO, combines with their silica setting free PbO, which is then reduced by the hot coke. The lead in all silicates is completely separated in the metallic state by iron. Any copper oxides in the charge will combine with sulphur, if sufficient be present, and form a matte, otherwise they will be reduced to copper which will alloy with the lead. Arsenic will be partly volatilized, but the greater part will form with the iron a speise which will contain copper, lead, silver, etc. Antimony will also be partly volatilized, carrying with it silver and lead, and part will enter the lead.

The following conditions are essential for successful smelting in the blast furnace :—

(*a*) The top of the charge should be cool and quiet.

(*b*) The charge should descend regularly.

(*c*) The minimum amount of coke should be used.

(*d*) Only so much of the iron should be reduced as will prevent an undue proportion of lead from passing into the matte and avoid the formation of accretions or " sows."

(*e*) The volume of air blown in must be carefully adjusted.

(*f*) Barren fluxes should be avoided whenever possible.

(*g*) The slag should flow easily and be clean.

The products of the smelting are :—

(*a*) Lead termed " base bullion " or " work-lead," which should contain the lead, silver, and gold present in the ores as far as these metals can be extracted.

(*b*) " A matte," which should contain as much as possible of the copper, and the remaining lead, silver, and gold.

(*c*) A speise, when arsenic is present in the ores, containing gold, silver, iron, and lead.

(*d*) A slag containing the other constituents of the ore which have not been volatilized.

(*e*) Flue dust and fume.

Work Lead or Base Bullion.—During the working of the furnace the lead rises in the basin at the top of the Arents' tap. In some large works it is allowed to overflow into a casting pot, which is mounted on trunnions on a bogie, so that it can be run on rails to the moulds into which the lead has to be poured The arrangement at the Selby Smelting Works (Cal.) is shown in Fig. 75.*

The moulds are water-cooled, being set in a shallow bosh through which water is circulated. At other works the work lead or base bullion is taken in tapping pots to 30-ton drossing kettles, where it is poled and skimmed before being cast into pigs. In small works it is laded from the basin into moulds, as already stated.

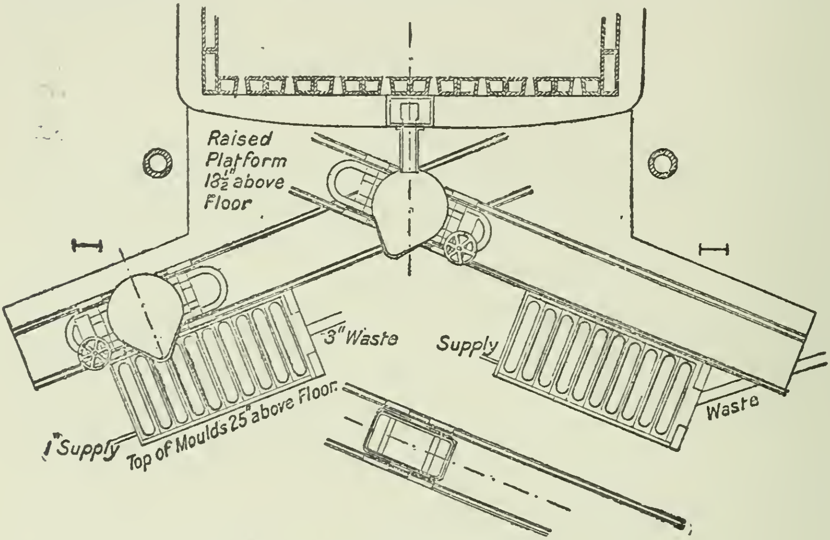
Raised Platform 13½" above Floor
3" Waste
Supply
Waste
1" Supply
Top of Moulds 25" above Floor

Fig. 75.—Arrangement of Casting Plant for Lead.

Blast-furnace lead contains the silver and any gold which may have been present in the ore. It is always more or less impure, copper, antimony, arsenic, and iron being nearly always present; the copper ranging from 0·1 to 0·8 per cent.; the antimony from 0·2 to 1·6 per cent.; and the arsenic from 0·1 to 0·4 per cent. The iron rarely exceeds 0·03 per cent. Zinc and bismuth also frequently occur, but only in very small quantities. Special care is necessary in taking samples for the assay of the metal, as the silver is very irregularly distributed in the pigs. Samples are taken during the casting of the pigs, and also from the pigs themselves when they have to be sold (see p. 221). The amount of silver present ranges from 0·15 per cent. at Laurium to 1·073 per cent. at Port Pirie.

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* *Eng. and Min. Journ.*, July, 1908

At Trail, B.C., the gold reaches 0·0122 per cent., but is usually very much less.

Handling of Slag and Matte (*and Speise when present*).—In small furnaces there is no fore-hearth, the slag, matte, and speise being tapped from time to time into deep conical pots, in which the matte and speise when present settle to the bottom in the order of their specific gravities, the speise forming the lowest layer ; but the separation is imperfect.

When cold the pots are inverted, the cakes of matte knocked off, as well as any foul slag, the latter going back to the blast furnace. An " overflow " pot is sometimes used. This is merely an extra large slag pot, into which the slag and matte flow continuously. The matte settles to the bottom, and the slag overflows at the top into an ordinary slag pot. As the matte accumulates it is tapped out. In large furnaces the slag, matte, and speise flow continuously into a fore-hearth or settler (see Fig. 74). The settlers closely resemble those used in copper smelting both in construction and mode of working (p. 106); in fact, any of them may be used for lead-smelting furnaces, their size depending on the quantity of matte produced daily. The above is the common method for the separation of these products, but a better separation is obtained by using a large reverberatory settling furnace, removed from the blast furnace, and heated by either coal or oil. These furnaces are in use at several of the chief smelting works, and yield a much cleaner slag than the ordinary settler.

The reverberatory settling furnace is usually of large size ; at the Arkansas Valley Works, Leadville, it has a capacity of about 100 tons. The clean slag is tapped from it almost continuously into slag pots on wheels. The matte is tapped from time to time and cast into flat cakes, so that it may be readily broken up ; and about once a day lead is tapped from a lower taphole.

The slag which overflows from the fore-hearth or settler may be received in slag pots, which are hauled to the dump by locomotives or otherwise ; or it may be granulated and washed away to the dump or trucks, as described under " Copper," p. 108. In many modern works, however, the slag from the fore-hearth is run into large slag pots of 2 or 3 tons capacity, which have a tap-hole near the bottom. At the dump, the slag is tapped out after standing a short time, the pot is then run back to the works, and the shell of solidified slag, which may contain small shots of matte, is emptied out and sent to the blast furnace.

Matte.—The matte produced in smelting lead ores containing copper is a variable mixture of sulphides in which iron generally predominates, but lead and copper are also present, and to a lesser extent Zn, Ni, Co, Mn, As, and Sb. The copper may range from about 2 to 20 per cent. or more ; lead from 5 to 20 per cent., and iron from 30 to 50 per cent. Silver is always present, the amount depending on the silver contents of the work-lead, and may reach 86 ozs. per ton. Ordinary lead mattes low in copper are usually but not always poor in gold. At the Globe Works (Denver) a matte with 12 to 15 per cent. Cu contained 0·05 oz. Au per ton ; but one at Dapto (N.S.W.) with about 4 per cent. Cu, but 47 per cent. Fe, contained 0·2 oz. per ton.

The matte, if poor in copper, is usually roasted and returned to the blast furnace until it becomes enriched to 12 or 14 per cent. If in sufficient quantity, it may be roasted and then smelted in a small blast furnace with siliceous fluxes or ores to a 40 to 50 per cent. matte, which can be shipped to copper smelters.

Lead Speise.—The speises produced in lead smelting are chiefly arsenides of iron, containing more or less sulphur, copper, and lead, much of the last being disseminated as shots. When the ore contains nickel and cobalt, these also are found in the speise. Speise always contains silver, but never in large percentages unless the lead is rich in silver. A speise at Pueblo had 4½ ozs., and one at Mapimi, Mexico, 44 ozs. per ton.

The gold contents are often high. When speise and matte are made together, the speise is poorer in silver but richer in gold than the matte.

Slags.—Their composition has been already dealt with.

Flue Dust.—See pp. 221, *et seq.*

Losses in Smelting.—They are chiefly due to losses in the slags and to volatilization.

In smelting ordinary ores in the blast furnace a total loss of 6 to 7 per cent. lead is good work, whilst 10 per cent. is not usually considered unsatisfactory, the lead assays being made in the "dry" way. The loss of silver will generally range from 2 to 4 per cent., whereas there is but little, if any, loss of gold.

The following are typical examples of lead smelting at modern works :—

The Bunker Hill Smelter and Refinery, Kellogg, Idaho.—In these works the furnace product is not shipped as lead bullion, but is treated further, the output being marketed as refined lead, silver, and gold. It was designed by Jules Labarthe to treat the concentrate obtained at the Bunker Hill, Sullivan, and Hecla Mills, together with crude ore from the Hecla and other mines. The supply is nearly all sulphide ore or concentrate which has to be roasted and about 10 to 15 per cent. of oxidized ore. The original plans were subsequently modified so that pulverized coal should be used instead of oil for heating the boilers, kettles, softening, and other furnaces. The arrangement of the plant is shown in Fig. 75*a*.

The ores after crushing and sampling are transferred by belt conveyors to any one of eight large storage bins, from each of which the correct proportion can be fed to a belt conveyor and delivered to the roasting department.

The blast furnaces are fed from 24 bins of 3,400 cubic feet capacity each, divided as follows :—Eight for roasted and sintered material and eight for limestone, crude ore, slag, by-products, etc., and eight for coke.

Each bin has two discharge-openings. Under each of these there is a 4-ton capacity hopper-scale, by which the various parts of the charge are weighed out and bedded in the hopper of the charge cars.

The roasting department contains seven 42-inch by 264-inch standard Dwight-Lloyd sintering machines, with pallets provided with self-cleaning grates ; also a seven-hearth Wedge furnace 21 feet in diameter. The latter is used to give the matte and high sulphur ores a preliminary roast, after which they are mixed with the regular Dwight-Lloyd charges of concentrate for final roasting and sintering.

The Dwight-Lloyd charges are made up to contain from 10 to 11·5 per cent. of sulphur. In order to make them sufficiently porous they are mixed

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[*] C. D. Rice, *Eng. and Min. Journ.*, July, September, October, November, 1918.

with jig middling, from the ore-dressing plant, which supplies most of the iron to the blast furnace

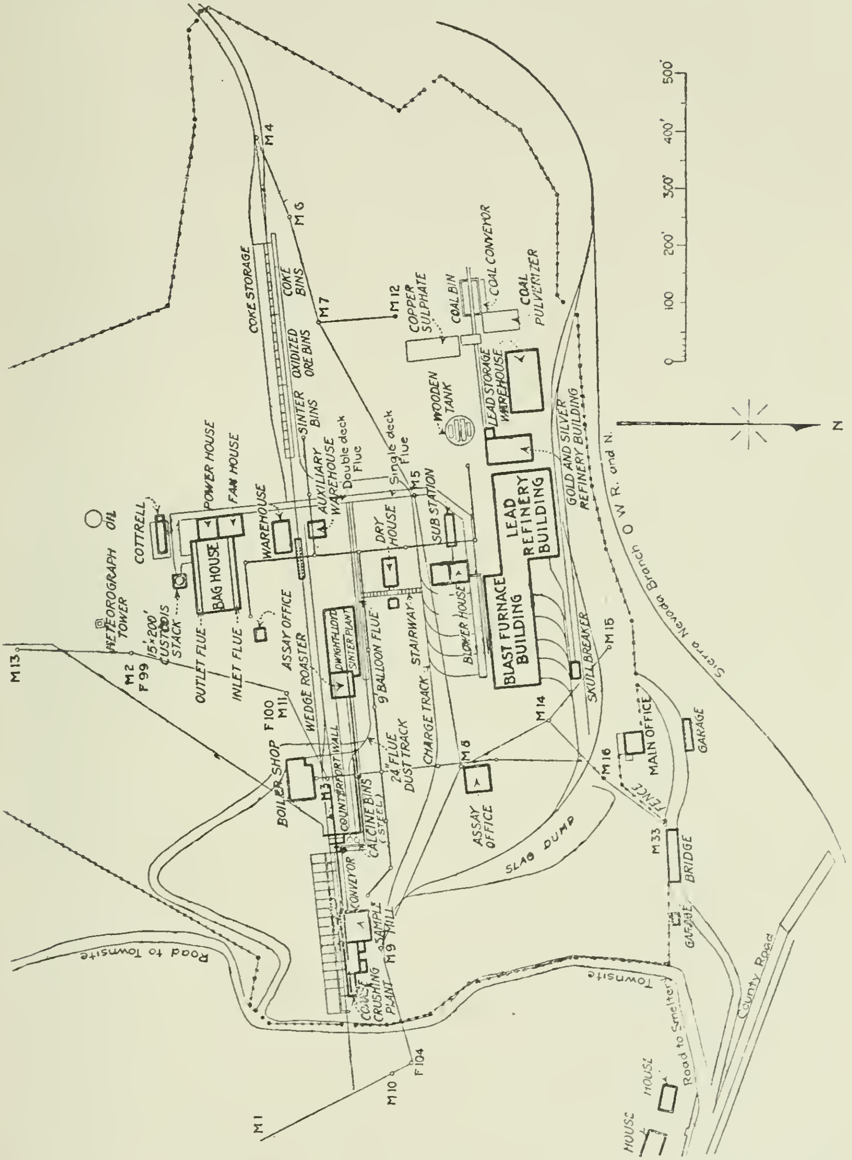
COKE STORAGE
COKE BINS
OXIDIZED ORE BINS
SINTER BINS
M 4
M 6
M 7
M 12
COPPER SULPHATE
COAL BIN
COAL CONVEYOR
COAL PULVERIZER
LEAD STORAGE WAREHOUSE
WOODEN TANK
AUXILIARY WAREHOUSE
Double deck Flue
Single deck Flue
M 5
SUB STATION
DRY HOUSE
LEAD REFINERY BUILDING
GOLD AND SILVER REFINERY BUILDING
O W R. and N.
Sierra Nevada Branch
POWER HOUSE
FAN HOUSE
WAREHOUSE
COTTRELL
OIL
BAG HOUSE
METEOROGRAPH TOWER
15'×200' CUSTODIS STACK
OUTLET FLUE
INLET FLUE
ASSAY OFFICE
WEDGE ROASTER
DWIGHT-LLOYD SINTER PLANT
9' BALLOON FLUE
STAIRWAY
BLOWER HOUSE
BLAST FURNACE BUILDING
SKULL BREAKER
M 15
M 13
M 2
F 99
F 100
M 11
COUNTERFORT WALL
24" FLUE DUST TRACK
CHARGE TRACK
M 8
M 14
M 16
MAIN OFFICE
GARAGE
FENCE
BOILER SHOP
M 3
CALCINE BINS (STEEL)
ASSAY OFFICE
SLAG DUMP
M 33
BRIDGE
CONVEYOR
SAMPLE MILL
M 9
COARSE CRUSHING PLANT
GARAGE
Road to Townsite
Townsite
Road to Smelter
County Road
HOUSE
HOUSE
F 104
M 10
M 1
0
100
200'
300'
400'
500'
N

Fig. 75a.—Arrangement of Bunker Hill Smeltery and Refinery.

In the blast furnace building there are four blast furnaces 48 inches by 180 inches at the tuyeres. Each furnace has twenty 4-inch tuyeres. The height of the furnaces from the centre of the tuyeres to the feed-floor is 20 feet

9 inches. The blast is supplied by two turbo-blowers, each having a capacity of 12,000 cubic feet of free air per minute at 48 ozs. per square inch pressure. The lead is taken by a launder to a ladle at the front of the furnace, and the slag is tapped into two settlers placed in series. The blast furnace building is continuous with the lead refinery building, and both are served by a 20-ton travelling electric crane. The settlers are small, the first being 6 feet in diameter and 3 feet 6 inches deep. The second 5 feet in diameter and 2 feet 6 inches deep. They are fitted with trunnions, and are removed by the crane when they begin to slag up and others put in. The matte is tapped from them into small ladles handled by the crane, which also takes the lead ladles and pours the lead directly into the drossing kettles of the lead refinery. The slag is run from the second settler into motor-dumping slag pots and taken to the slag dump, the slag shells being returned to the blast furnaces.

The furnace charge contains from 35 to 40 per cent. of Pb and 1 to 3 per cent. Zn, and is mixed so as to obtain a slag containing 32 per cent. FeO, 2 to 4 per cent. ZnO, 32 to 33 per cent. SiO_2, 16 per cent. CaO, and incidentally 3 per cent. MnO.

The capacity of each furnace ranges from 200 to 250 tons of ore smelted per 24 hours.

In the lead refinery there are two drossing kettles having a capacity of 50 tons each. In these the lead feed for the softening furnaces is accumulated and the dross taken off is returned to the blast furnace charge.

After this operation, the molten metal is sent by a centrifugal pump through pipes to one of two softening furnaces, each having a capacity of 80 tons, and fired with powdered coal. At the softening furnace the molten bullion is raised to a temperature between 593° and 649° C., when the antimony is drossed off together with some of the lead. The operation takes from 10 to 24 hours. This dross is converted into hard lead.

From the softening furnaces the lead bullion flows by a launder to the 50-ton desilverizing kettles, of which there are four, where it is treated by the Parkes process.

The zinc is mixed with the lead by means of a motor-driven Howard's stirrer, and the skimmings are squeezed in a Howard press. The skimmings are charged into the retorts of Faber du Faur furnaces, of which there are eight, in which the zinc is distilled off. The lead-silver-gold bullion, which is left, is poured into bars and sent to the cupel furnace. The silver-gold bullion remaining after cupellation is poured into flat bars, which are parted by the ordinary sulphuric acid method (see p. 359) and gold and silver bullion obtained.

The lead after treatment by the Parkes process contains between 0·5 and 0·6 per cent. zinc, and is heated in one of two refining furnaces, each having a capacity of 80 tons, and fired with pulverized coal, in which the zinc is removed. From these the refined lead goes by steel launders to one of the four 50-ton merchant kettles. From this it is sent by a centrifugal pump to a Miller casting machine, where it is moulded into 100-lb. pigs. The dust and fume from the whole plant is treated as follows :—The gases from the blast furnaces are taken by down-comers to a brick flue and sent by means of fans to a bag-house, and thence to the stack.

The bag-house, which is 130 feet long by 56 feet wide, contains 1,200 bags, 18 inches in diameter and 30 feet long, and is divided into three main sections. Under the nipple floor each section is divided into four compartments, each with an independent damper to facilitate cleaning.

The gases from the roaster building, the various refining furnaces, and kettles are led to a special house, where they are treated by the Cottrell system of precipitation.

The Sulphide Corporation Smelting Plant at Cockle Creek, New South Wales.*—" This plant treats annually 200,000 tons of materials and produces 31,000 ozs. of gold, 2,500,000 ozs. of silver, 28,000 tons of soft lead, and 320 tons of antimonial lead. In addition, it furnishes 19,000 tons of chamber-acid, 30,000 tons of super-phosphate, and 800 tons of ammonium sulphate. All ores carrying over 3 per cent. S go to the roasting department. A typical roasting charge contains Pb 50, SiO_2 7, FeO 7·5, MnO 2·3, ZnO 10, CaO 6, S 15 per cent. Ten gas-fired Godfrey furnaces, 21 feet in diameter, treat per day 300 tons of charge and reduce the sulphur content to 9·5 per cent. The rough-roasted product is blown in 24 5-ton Huntington-Heberlein cast-iron pots of an elliptical form. The ore, dull red from the roasters, is dumped into the pots and blast with a pressure of from 10 to 12 ozs. turned on.

" No fire is kindled in the pot, nor is any separate kindling charge made. From six to eight hours are required to finish an operation. The hood of a pot has two gas pipes. One conveys gas suitable for acid-making into the gas main leading to the sulphuric acid chambers, the other leads unsuitable gas to the chimney stack. About 80 per cent. of the SO_2 is converted into H_2SO_4. The sintered cake is dropped on the floor, 10 feet below, is sprayed, and broken by hand into 6-inch lumps. The pots are hung on hollow trunnions, through which the air blast passes down a pipe outside the pot to the wind box. There is, therefore, no necessity for detaching and reattaching the air-pipe after each tipping of the pot. The smelting division has three blast furnaces, two for ore and one for antimony slag and other intermediaries free from silver. The blast is supplied from two sets of vertical piston blowers, each capable of delivering 8,000 cubic feet of air per minute at a pressure of 60 ozs. per square inch.

" One ore furnace is 11 feet 6 inches by 5 feet at the tuyeres and 35 feet 9 inches high from tapping to feed floor, has thirteen 3-inch tuyeres, works with a blast pressure of 60 ozs., smelts in 24 hours 300 tons of charge, exclusive of return slag, and produces 100 tons of lead bullion. The cast-iron forehearth mounted on wheels is exchanged several times a shift. The lead is tapped into small cast-iron pots and sent to the drossing furnace, a small reverberatory of about 7 tons capacity. The dross is transferred to a liquating furnace, where most of the lead is sweated out and returned to the drossing furnace. The dross is then allowed to accumulate till there is sufficient to warrant No. 3 furnace being blown in.

" The lead from the drossing furnace is tapped into two rings of 100 moulds each, which revolve on their own axes. The bars then go for treatment in the refinery.

" The other ore furnace is 8 feet 2 inches by 4 feet 4 inches at the tuyeres and 34 feet high, has nine 3-inch tuyeres, works with a blast pressure of 55 ozs., and smelts 250 tons of charge in 24 hours.

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* H. O. Hofman, *Eng. and Min. Journ.*, January, 1920. Abstract of Paper by Guy Courtney read at the Meeting of the Australasian Institute of Mining Engineers, August, 1918.

"The third furnace is 5 feet 6 inches by 2 feet 9 inches at the tuyeres.

"The great height of the ore furnaces, which have a working height of about 28 feet, and the consequent high-pressure blast, is a striking feature. The charge contains about 75 per cent. of H-H material. The slag made assays Pb 0·7, FeO 36·4, MnO 16, CaO 17·2, SiO_2 24·5, ZnO 12·0 per cent.; here the low percentage of SiO_2 is noticeable."

Silver-Lead Smelting at Laurium, Greece.*—The blast furnace is of the American type, and handles from 250 to 300 metric tons per day. It measures 150 by 44 inches at the tuyeres, and 20 feet 4 inches from tuyere level to feed floor.

The crucible of the blast furnace is built as usual of fire-brick, but inside is a lining of a special chrome-magnesia brick containing 3 parts of burnt magnesite to 1 part of chromite, this being necessary on account of the speise made here rapidly corroding all ordinary fire-brick, whether siliceous or basic, having, however, but little effect on those made of the above mixture.

Special attention may be directed to the arrangements for handling matte and slag, one interesting feature of which is the employment of a fore-hearth having a constant flow of slag without a trap spout. The slag, matte, and speise leave the furnace at one end, through a tapping jacket of phosphor-bronze, and the minimum aperture of which is 2¾ inches in diameter. Exactly opposite the centre of this aperture a long water-cooled plug is held in glands, hanging from fixed supports in such a way that it can be pushed in or drawn out at pleasure, thus restricting or enlarging the area of the annular ring left between its rounded point and the tapered hole in the tap-jacket, through which the molten products of the furnace issue. The plug is a water-cooled steel tube with rounded point made of wrought copper.

By entering or withdrawing the plug, irregularities in the slag-flow caused by variations in the speed of smelting or in the pressure of blast are controlled with great exactitude, so that neither do the tuyeres become slagged, nor is there any escape of blast at the slag-spout.

The matte and speise are tapped together from the fore-hearth, usually once in twenty-four hours. The slag falls into a cast-iron launder, where it meets a stream of water and is granulated. The lead overflows from the Arents siphon tap into one of two steel drossing pots, holding 2,500 kg. In these it is drossed and tapped at intervals into the usual half-circle of moulds on wheels. With a fuel consumption of 13 per cent. of coke, the furnace puts through from 275 to 300 metric tons per twenty-four hours of a self-fluxing charge carrying about 11 per cent. lead. Blast is supplied by either of two Roots' blowers, each of which can deliver 10,500 cubic feet of air against a pressure of from 35 to 40 ozs.

Salida, Colorado.†—Oxide and sulphide lead ore and clinkered residue from zinc retorts are treated. The oxide ore is screened, the fine going to the sintering plant and the coarse to the blast furnaces.

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* *Eng. and Min. Journ.*, May, 1909.

† *Min. Ind.*, 1913, p. 461.

The sulphide ores go to two Godfrey furnaces, each treating 25 tons per day, and one Wedge furnace treating 75 tons.

The product from this preliminary roasting is sprayed with water, and mixed with oxide ore, etc., to bring the percentage of sulphur down to 15 per cent. It is then blast-roasted in four Dwight-Lloyd machines, 42 by 264 inches, each treating 80 tons per day.

There are two blast furnaces, 48 by 100 inches, and four 44 by 144 inches, all being 17 feet 6 inches high from tuyere to feed floor.

The lead is taken in ladles to drossing pots of 39 tons capacity, where it is agitated with compressed air, skimmed into a Howard press, and siphoned into bars for shipment, after having been sampled by dips, each weighing about 0·5 assay ton. There were frequent discrepancies in the assay samples as regards the content of silver and especially of gold, but they disappeared when the following procedure was adopted, the temperature being determined by a pyrometer :—" Take off heavy dross at 900° F. ; blow until temperature reaches 680° F., skimming from time to time ; raise the heat to 720° F. for sampling, and mould at 800° F. Since this method was adopted there has been little trouble."

Experiments in the Hydrometallurgy of Lead.*—New methods of treatment of lead ores, be they dry or wet, usually do not get beyond the experimental stage, but two recent modes of procedure studied in the laboratory of the Bureau of Mines at Salt Lake City may form an exception to the general rule. One method gives low-grade oxide lead ore a chloridizing roast in a reverberatory or blast-roasting furnace at a temperature of 850° to 900° C., with the aim of volatilizing the chlorides of lead, gold, and silver formed, which are collected in a dust chamber supplemented by a Cottrell electrostatic precipitator. The extractions obtained on a small scale reached 99 per cent. of the lead and from 80 to 90 per cent. of the gold and silver. With sulphide ore the lead is readily volatilized, but not the precious metal ; this remains behind and has to be recovered by lixiviation. The other method involves the lixiviation of raw oxide lead ore with saturated brine acidified with sulphuric acid, and the recovery of this lead either by electrolysis or by precipitation with burnt lime. Extractions of lead varied from 80 to 98 per cent., depending upon the amounts of lead present as sulphide.

Experiments at Kellogg, Idaho, with sulphide lead ore, involving chloridizing in a Holt-Dern blast roaster and leaching with acidulated brine, gave a yield of lead of 85 to 95 per cent., and of silver of 80 to 90 per cent.

Flue Dust and Lead Fume.—In the blast-furnace smelting of lead ores ; in fact, in all operations in the metallurgy of lead, in which the ores or metal are exposed to a high temperature, either flue dust or lead fume, or both, are produced in considerable quantities. They are often included under the term " flue dust," but they are really two distinct kinds of material.

Flue dust consists of fine particles of ore, fuel, and fluxes which have been carried over mechanically, and is found chiefly in the flues or condensing chambers nearest the furnaces. Small amounts of lead oxide and sulphates are also present.

Lead fume, on the other hand, consists chiefly of lead sulphate, lead oxide, with zinc oxide, arsenical and antimonial compounds of lead, if zinc, arsenic, and antimony are present in the ore or metal treated. It is found principally in the flues and chambers further away from the furnaces, and some always escapes condensation and collection, and passes into the air through the chimney stack.

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* H. O. Hofman, *Eng. and Min. Journ.*, January 12, 1918.

The collection of flue dust proper is comparatively easy, and can be effected by diminishing the velocity of the furnace gases by making the flues large, and by constructing settling chambers of considerable capacity. The particles of true lead fume, however, can be thus only partially settled.

The fume being in a state of extremely fine division is, notwithstanding its high specific gravity, kept long in suspension in the flue gases, and the condition which seems to be the most favourable for its deposition is that of the least movement of these gases. Accordingly, at all the older lead works we find capacious flues of extraordinary length.

Thus at Freiberg the flues have been added to till they are now 5 miles in length ; and at Bagilt, Flintshire, their length is about 2 miles.

In nearly all modern works the construction of these very long flues is impracticable, and other arrangements have to be adopted, yet in constructing even a modern condensing and collecting plant advantage may be taken of the slope of a hill, when possible, the flues being led up it in a zig-zag manner.

The conditions which are essential to the successful condensation and collection of lead-fume are :—

1. The furnace gases must be cooled, as hot particles do not attract one another.
2. The velocity of the gases must be reduced.
3. As large an area of surface as possible, on which the fume can condense, should be presented to the gases. It should be borne in mind in this connection that a cold and dry surface attracts the particles, whilst a hot and moist surface repels them more or less.

The various methods of condensing and collecting flue dust and fume may be classified in two divisions—namely, dry and wet.

Dry methods are almost universal. Wet methods are, as a rule, imperfect and costly in working.

Dry Methods.—These comprise—

1. Flues of great length.
2. Flues supplemented by dust chambers or a bag-house or by both.
3. The Cottrell system of electrical precipitation.

The simplest method is to have large flues, as long as possible, supplemented by capacious chambers, but these alone are insufficient, and in all modern works the arrangments are more elaborate. It is, however, of great importance that all flues should have a large cross-section.

Baffle walls in the flues have been given up, but they are still found in the chambers where these are in use.

Both flues and chambers are best built of red brick, and where the gases contain much SO_2 overburnt bricks, if procurable, should be used.

Re-inforced concrete has been used, but has been largely given up owing to its liability to crack, and to be attacked by the furnace gases.

Where space is limited, zig-zag flues, as at Cordoba, and spiral flues at Bagilt, have been constructed, as then one wall, except at the extreme outside, serves for two flues.

The cooling, which is effected in the main brick flue, is sometimes supplemented by means of a sheet-iron circular flue of large diameter, up to 15 feet, or of the form shown in Fig. 76, with pockets at suitable intervals; but in the cooler parts of the system the iron is liable to be corroded by the acid in the gases. Cooling is necessary, because, as has been pointed out, the particles when hot repel one another and will not collect together. Baffle walls are used in the chambers, in order to present a large surface for the particles to deposit upon, but increased surface has also been obtained by the use of Freudenberg plates and Rösing wires in the flues. Neither of these has, however, found much favour in America. Freudenberg plates are thin sheet-iron plates which are suspended in the flues longitudinally at about 3½ inches apart. The fume settles on them, and when it has attained a certain thickness falls to the bottom of the flue. They retard the draught, however, and are said not to act satisfactorily except between 50° and 70° C. They are, too, rapidly corroded below 50° C.

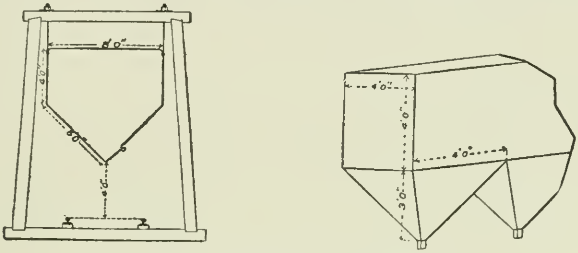

Fig. 76.—Sheet-Iron Cooling Flue.*

Rösing wires are wires suspended in parallel rows from a wire netting at the top of the flue. At the works of the Boston and Montana Company, where they have been introduced, the wires are of Nos. 10 and 12 wire gauge, and 20 feet long.

Simple flues and dust chambers of large capacity are most common in America for condensing and collecting the flue dust and fume, and, when possible, they are built at such a height that cars, to receive the dust, can be run below them under hoppers which are placed at suitable intervals.

A high chimney stack is necessary to draw the furnace gases through the above-described plant, especially where Freudenberg plates are employed; in some works a Guibal fan is in use to supplement the chimney draught.

The amount of lead and silver in the material taken from the flues and condensing chambers varies according to the richness of the ore in these metals, the former will, on the average, range from 25 to 40 per cent., and the latter from 13 to 22 ozs. per ton. The above methods, however, fail to condense and collect a considerable amount of the true lead fume, so that in large works they are generally supplemented by filtering the gases through cotton or woollen bags arranged in a suitable chamber or "bag house."

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* Collins, *op. cit.*, p. 340.

In Dr. Percy's *Metallurgy of Lead*, p. 449 (1870), we find the following statement:—

"I am convinced from many other experiments that, except for the difficulties arising from the heat and sulphurous acid, it would be possible to construct some textile fabric through which the smoke might be slowly forced or drawn, leaving the bulk of the fume on one side."

He was, hence, the first to suggest filtration, but Lewis and Bartlett were the first to apply it on a practical scale, and the process bears their names.

The standard bag house is a large room in which the bags, of which there are several hundreds, are suspended (Fig. 77). The bags are simply tubes of cotton or woollen cloth commonly about 30 to 35 feet long and 18 to 20 inches in diameter. If the gases are moderately rich in SO_2 the bags should be of woollen material, otherwise they may be of unbleached calico. The bag house is divided by partitions into sections, so that any section can be shut off for the purpose of cleaning. The furnace gases, after having been cooled to about 82° in the flues and chambers described above, are forced by means of a fan into brick chambers 12 to 14 feet high below the floor of the bag house. The lower ends of the bags are secured to openings in the floor above the chambers, and when the bags are shaken the lead fume falls into the chambers. The upper ends of the bags are closed, being tied up by the cords by which they are suspended. The gases pass up and through the bags, leaving the lead fume inside, and into the air through the ventilators shown in the figure, or sometimes through steel chimney stacks.

An improvement in the old method of mechanically shaking the bags has been recently introduced. It consists in cutting off a chamber from the distributing flue and connecting it with the chimney stack, or producing a suction in it by other means. This causes the bags to collapse and discharge their flue dust.

The lead fume, when sufficient has accumulated, is ignited on the floors of the collecting chambers, producing a grey cinder, which at the Globe Works (Denver) contains as oxides and sulphates Pb 75 per cent., Zn 3 per cent., Fe 0·5 per cent., As 1·3 per cent., and Ag 4 ozs. per ton. The fumes from roasting furnaces, although rich in lead, are most destructive to the bags, owing to the SO_3 present, unless they are largely diluted with the blast-furnace gases. At the Bingham Junction Works a method of neutralizing the acid, by blowing zinc oxide into the flues, has been introduced, it is said, with success. The flue dust from the flues is commonly briquetted with slaked lime, or clay, and sent to the blast furnace. The fume from the bag house after ignition is in the form of a sintered mass suitable for the blast furnace.

The bag house at Selby (California) is constructed of re-inforced concrete. An excellent description of it is given in the *Eng. and Min. Journ.*, Sept. 1908.

As regards the economy of bag-house filtration, it has been found that, when the ores smelted are poor in lead and the precious metals, the cost is greater than the value of the metals saved ; on the other hand, when the ores are of high grade, the use of a bag house is profitable. When, however, the works are in the neighbourhood of farms and villages, they are necessary to avoid litigation.

The Cottrell Process.—For a description of this process, see p. 108. It has been in use for several years at the lead works of the Selby Smelting Company, California, and recently has been installed in the lead division of the Consolidated Mining and Smelting Company, Trail, B.C. The condensation plant* at the latter works, which treats 100,000 cubic feet of gas

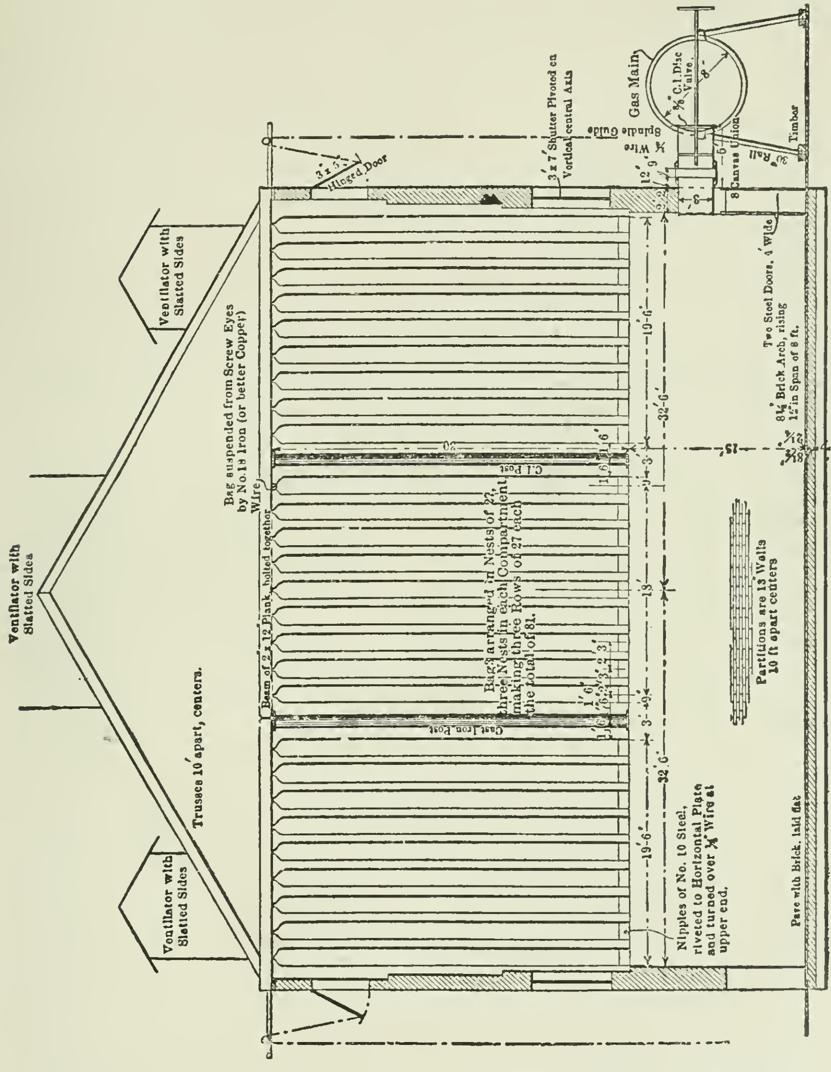
Ventilator with Slatted Sides
Ventilator with Slatted Sides
Ventilator with Slatted Sides
Trusses 10' apart, centers.
Bag suspended from Screw Eyes by No.18 Iron (or better Copper) Wire
Beam of 2 x 12 Plank, bolted together
3' x 5' Hinged Door
3' x 7' Shutter Pivoted on Vertical central Axis
Gas Main
3/8 C.I.Disc Valve.
8'
¾ Wire
Spindle Guide
Canvas Union
30# Rail
Timber
C.I Post
Cast Iron Post
Bags arranged in Nests of 27, three Nests in each Compartment making three Rows of 27 each the total of 81.
Two Steel Doors, 4' wide
8½ Brick Arch, rising 12" in Span of 8 ft.
Partitions are 13" Walls 10 ft apart centers
Nipples of No. 10 Steel, riveted to Horizontal Plate and turned over ¼" Wire at upper end.
Pave with Brick, laid flat
19'-6"
32'-6"
13'
19'-6"
32'-6"
12'
12'-9"

Fig. 77.—Bag House, Globe Smelting Works. (*Eng. and Min. Journ.*, July 1905.)

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* *Min. Ind.*, 1916, p. 469.

per minute, contains 384 vertical pipes 12 inches in diameter and 16 feet long. A rectified current of 75,000 volts passes through the central wires; the flue dust collected, which amounts to 8 tons per day, averages 70 per cent. of lead.

Wet Methods.—The chief drawback in carrying out the wet methods is the resistance which the fine particles of the fume offer to being wetted, so that it is difficult to bring them into intimate contact with the water.

One of the best methods, especially if space is very limited, as at works in towns, is that of the Sheffield Smelting Company; but very powerful blowers are required. The furnace gases are first cooled to about 49° to 54° C. by passing through flues and iron pipes. They are then forced, by means of Roots' blowers, into an iron tank in which a number of wire-gauze diaphragms are arranged horizontally, one above another, at small distances apart, and submerged in water. The gases are distributed under these diaphragms by means of a series of iron pipes, forced through them, and thus brought into intimate contact with the water.

At Monteponi, the fumes whilst hot are passed through a chamber with longitudinal and transverse baffle walls, by which their direction is changed six times, and each time they are struck by a fine spray of water.

Bag Filtration at the Murray Plant, Utah.*—The Murray bag house was put into operation in 1907. The outside dimensions are 216 feet 6 inches by 90 feet 6 inches, the height to roof trusses being 51 feet 6 inches. It is constructed of brick.

The bag house is completely divided into four compartments by means of brick partitions running from the floor line to the apex of the roof. Each of the four compartments has a steel stack, 6 feet in diameter by 78 feet high, coming out from the apex of the roof, about the centre of the compartment.

Below the floor, carrying the steel "thimbles" to which the bottoms of the bags are attached, each compartment is divided into four chambers or cellars by means of brick partitions.

A distributing flue, 16 by 16 feet, built of brick, runs the entire length of the bag house, and connects with each of the sixteen cellars by means of 42-inch bull's-eye valves, made of ¼-inch sheet steel stiffened by angle irons.

On top of this distributing flue is a smaller flue, 11 by 16 feet, running the entire length of the bag house, and connected to each cellar by means of 34-inch bull's-eye valves.

This upper flue is connected to the bag house fan flue by means of a 6-foot sheet-iron downtake containing a butterfly damper, and is used to conduct the gases from any chambers that are in the sintering process back to the fan, and thence into the distributing flue. The bags are woollen, and are 18 inches in diameter and 30 feet long. There are 570,012 square feet of surface provided for filtering 165,000 cubic feet of gas per minute, or at the rate of 3·45 square feet of filtering surface per cubic foot of gas per minute.

The blast-furnace gases are conducted through 795 feet of brick flue and 70 feet of sheet-iron goose-neck; 725 feet of this brick flue is 16 by 17 feet; 70 feet of the brick flue is 16 by 20 feet. The sheet-iron goose-neck is 20 feet in diameter, made of ¼-inch steel. Back of the blast furnaces is 262 feet of 16 by 20 feet flue with sloping bottom. An exhaust fan with impeller 6 by 15 feet brings the gases from the blast furnaces, and forces them into the distributing flue, and through the bags. The gases discharge from the fan into the distributing flue, the lower bull's-eye valves being open, the gases enter the sixteen cellars, filter through the 4,032 bags, and discharge through the four steel stacks on the top of the bag house. Once every twenty-four hours all the bags are shaken. When the dust has accumulated to a thickness of about 24 inches, a compartment is closed off from the distributing flue, the cellar doors and valves connected with the return flue are opened, and fume in the four cellars is lighted by means of hot coals.

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* *Eng. and Min. Journ.*, October, 1912.

Desilverization, or the Extraction of Silver from Lead.

Three processes are followed, viz.:—

(1) Desilverization by crystallization. The Pattinson process.
(2) Desilverization by means of zinc. The Parkes process.
(3) Cupellation which follows the above.

Formerly all silver was extracted from lead by cupellation, but cupellation can only be profitably carried on now when the lead contains considerable amounts of silver.

By the Pattinson process silver is extracted with profit at Cordoba from lead containing only 14 ozs. per ton.

The Pattinson process is based on the fact that, when molten lead is slowly cooled, the crystals which form contain less silver than the remainder of the lead which remains fluid. Lead from pure ores—that is, "soft" lead—can be treated directly by the Pattinson process, but work lead, such as that usually produced in the blast furnace, and that from impure ores in the reverberatory furnace, must have a large proportion of the impurities removed by a process termed the "softening" or "improving" process, before it can be subjected to desilverization; as most of these impurities interfere with the operations. In the Pattinson process the effect of small quantities of antimony, arsenic, and copper in the lead is to make the crystals smaller and cause the production of much dross. As more time is required to drain small crystals than large, the period of drainage is prolonged, and the richer liquid lead sets in part on the surface of each crystal, and so is carried over into the poorer pot. Zinc is rarely present, but, if so, the crystals become richer than the fluid lead. Any bismuth present will be concentrated in the rich lead.

Copper is injurious in the Parkes process, as it retards the operations and consumes zinc, but is not specially injurious in the Pattinson process.

Softening Lead.—The impurities to be removed are sulphur, copper, tin, arsenic, and antimony. The operations of "softening" are carried on in a reverberatory furnace with a shallow rectangular bed, lined with fire-bricks, set in a large flat-bottomed mild-steel pan, and having the upper part of its sides surrounded by a water-jacket. They are usually of large capacity, taking charges of 30 to 100 tons or even more. By the introduction of machine charging the capacity of these furnaces has been recently increased to 240 tons.* An endless belt elevates the pigs, and drops them into a shoot down which they glide into the furnace through a hole in the roof.

The Softening Furnace.—The construction of a typical furnace at Port Pirie Works is shown in Fig. 78. Dimensions of hearth, 14 by 8 feet; of fireplace, 7 feet 4 inches by 2 feet 2 inches. The hearth is built of fire-brick enclosed in a pan of mild steel plate to prevent leakage of lead. The whole rests on transverse rails supported by brick walls running longitudinally. At the level of the lead is a water-jacket of mild steel of the form shown in the figure. There are three working doors on each side of the furnace. The fire-bridge is cooled by an air space, which runs from one side of the furnace to the other. The working bottom is built of two courses of fire-bricks closely set together.

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* E. F. Eurich, *Int. Cong. App. Chem.*, 1912, vol. iii., p. 79.

The water-jacket is necessary to prevent excessive corrosion of the sides by the metallic oxides formed in the operation. This corrosion is greatest at the level of the lead, hence the water-jacket is placed there. The capacity of the furnace is about 36 tons.

American furnaces are very similar to the above, the chief difference being that the water-jacket forms part of the sides of the pan in which the hearth is built.

The Softening Process.—The process consists of two, or of three stages if tin is present. In the first, the lead is very slowly melted down at a low heat and well stirred, when most of the copper is removed as a pasty dross consisting of a mixture of lead, copper, sulphur, arsenic, etc., which rises to the surface and is skimmed off. This part of the process is termed "drossing."

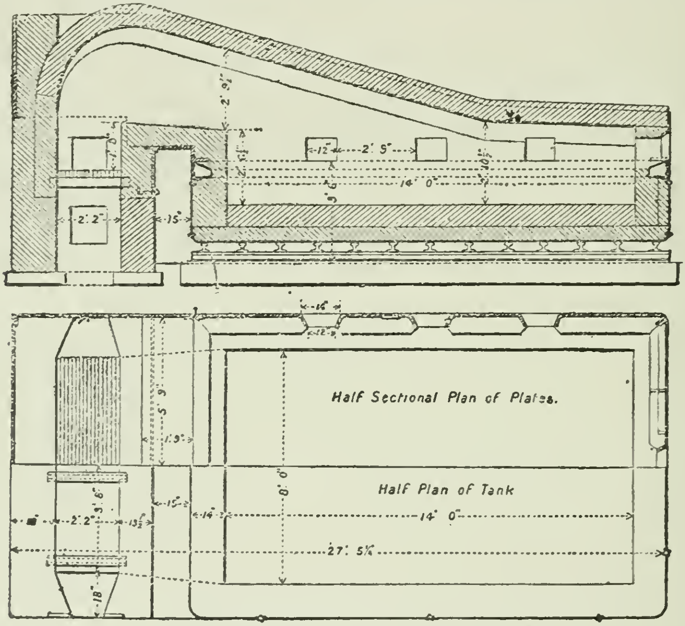

Fig. 78.—Port Pirie Softening Furnace.*

During the second stage the temperature is increased, the metal being freely exposed to the air, when a dry tin scum, if tin is present, containing some arsenic, forms and is raked off.

In the third stage, the antimony and remainder of the arsenic and other metals are oxidized; their oxides dissolve in the litharge, and are skimmed off from time to time. In this stage the temperature is again raised when lead antimonate appears as brownish-black oily drops, which gradually cover the surface of the lead, and is skimmed off with the aid of lime or ashes. Some of the arsenic and antimony are also removed by volatilization.

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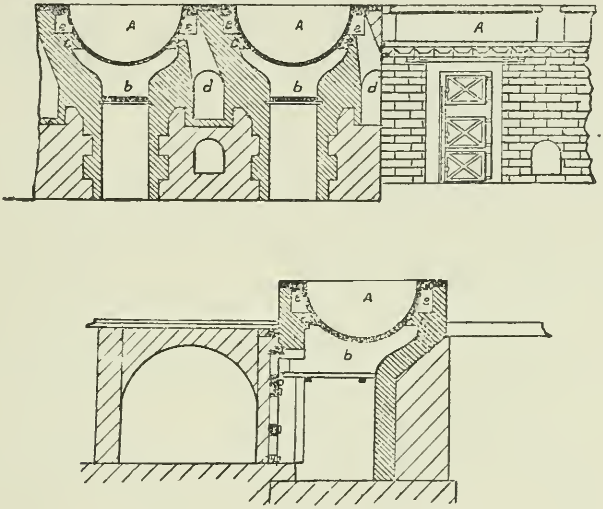
* Collins, *op. cit.*, p. 368.

Finally, the skimmings consist of yellow litharge only.

The time required for softening depends on the amount and nature of the impurities in the lead, and ranges from fourteen hours to two or three days. The presence of much antimony seriously retards the operation. Towards the end of the process a sample is taken, from time to time, by casting a small ingot, and allowing it to cool after its surface has been cleaned by drawing over it a piece of wood ; it should then present a fine indigo-blue colour.

After softening, the lead is cast either direct into iron moulds, or is first tapped into a large pot, in which the lead cools down to the proper temperature before casting. In casting the pigs, 40 or 50 moulds are arranged in a semicircle in front of the furnace or pot, so that they can be filled by means of a radially moving pipe which leads from the taphole, or by a siphon or other appliance. In works where the Parkes process is in use the lead is tapped direct from the softening furnace into the desilverizing pan or " kettle."



Figs. 79 and 80.—Pattinson Pots.*

The Pattinson Process.—The process is conducted in two distinct methods —viz., the Hand-Pattinson and the Steam-Pattinson process—but the principle on which each is based is the same—viz., when " softened " molten lead is slowly cooled the crystals which form are less rich in silver than the lead which remains fluid. The effects of impurities which interfere with the process have already been mentioned on p. 227.

The Hand-Pattinson process is conducted in a series of cast-iron pots or " kettles," eight to sixteen in number, arranged in a row, each being set over its own fire as shown in Figs. 79 and 80.

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* Collins, *op. cit.*, p. 387.

The pots vary in capacity from 8 to 15 tons.

At Bagilt (N. Wales) the pots were 5 feet 3 inches in diameter and 2 feet 9 inches in depth, and held 12 tons, but only 10 tons were charged. They were arranged in two series of nine each.

The process is carried on in two systems—the system of "thirds" and the system of "eighths." In the former, two-thirds of the lead is removed in crystals and one-third left in the pot. The lead left in the pot will be approximately twice as rich in silver and the crystals one-half as rich as the original lead. In the latter system, seven-eighths of the lead is removed as crystals, and one-eighth left in the pot, which will be approximately three times as rich as the original lead.

The system of thirds is that which is in practically universal use. It is conducted as follows:—

The pigs of lead are placed in the "charging" pot, which may be near the middle of the series, but its position depends on the amount of silver in the lead. They are melted and any dross which forms is removed with a perforated shallow ladle. The metal is then allowed to cool slowly, by removing the fire wholly or partly, and the crusts which form at the sides are detached and pushed down into the metal where they melt again.

The metal is continuously stirred until it becomes a kind of lead "mud," consisting of crystals and fluid lead. The crystals are now removed with a perforated shallow ladle, allowed to drain, and transferred to the next pan on the right. The ladle is suspended by a chain, and is jerked three or four times on a pig of lead resting on the side of the pot to promote the drainage of the liquid lead.

Two-thirds of the lead is thus removed as crystals. The liquid lead is then laded into the pot on the left.

The lead in the pots on the right and left is then successively similarly treated until the last pot in the series on the right, the "market pot," contains lead with only 10 dwts. of silver per ton, or generally less, and the last pot on the left, lead with 300 to 500 ozs. per ton.

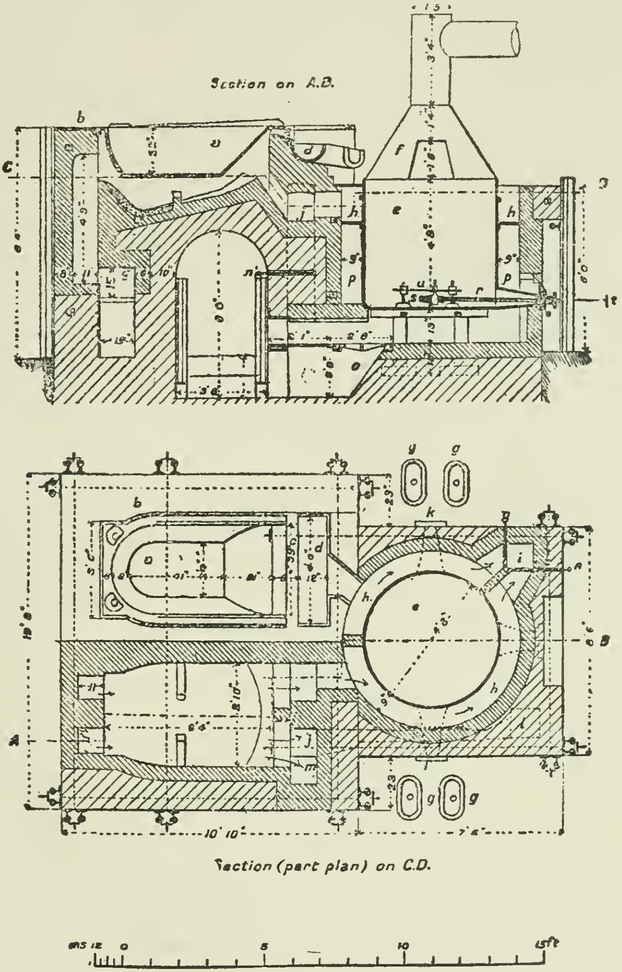
The enrichment of the lead cannot be carried beyond 650 ozs. silver per ton. The different pots at each stage have to be filled up with lead of approximately the same content of silver as that which they respectively contained before crystallization.

One fact of considerable practical importance in this process is that the foreign metals which may be present in the lead are to a certain extent concentrated in the enriched portion, so that the "market lead" produced is very soft and pure. Bismuth is specially concentrated in the enriched portion of the lead, and at Freiburg, where the work lead contains this metal, it is recovered from the litharge obtained in cupelling the rich lead.

Steam Pattinson Process—Luce and Rozan Process.—This process was invented by Luce and Rozan, to reduce the very hard labour of the hand process, and is now in use at several important works, as at Newcastle-on-Tyne, Przibram, Marseilles, Eureka (Nevada), and elsewhere.

As compared with the hand process, its disadvantages are greater cost of plant and repairs, but its advantages, which largely outweigh these, are less labour, less fuel, moderately impure lead can be used without a preliminary softening, and the resulting market lead is said to be softer.

The plant in use at Przibram is shown in Figs. 81 and 82. There are two cast-iron melting pans *a a*, each holding 7 tons of lead, a crystallizing pan *e*, holding 20 tons, and two large cast-iron moulds, each holding over 3 tons, for receiving the liquid lead from the crystallizing pan. The melting pans and the crystallizing pan are each heated by its own fire. The contents of the melting pans are poured into the crystallizing pan by lifting their hinder ends by means of a crane.


Section on A.B.
a
b
c
d
e
f
g
h
p
r
o
n
k
i
j
m
C
D
A
B
Section (part plan) on C.D.
ins 12 0 5 10 15ft
10' 10"
7' 6"

Figs. 81 and 82.—Steam Pattinson Plant* (Przibram).

The crystallizing pan is covered by a hood, to carry off the steam and fumes. It has a taphole at the bottom of one side, over which a perforated iron strainer is fixed, to keep back the crystals when the liquid lead is run off into the moulds. On another side, near the bottom, is the inlet for the steam pipe, which delivers the steam through a nozzle that can be opened or closed by a plug manipulated by a long iron rod. The steam is delivered below a perforated diaphragm or baffle plate, in order to distribute it. The system of working is by thirds.

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* Collins, *op. cit.*, after Hofman, *Metallurgy of Lead*, 1906, p. 448

Process.—The lead is first melted in one of the melting pans, drossed, and poured into the crystallizing pan, which already contains about 13½ tons of melted crystals from the previous charge. Steam is introduced for about two minutes, and the dross formed removed. The fire is now withdrawn, and steam, which must be dry and have a pressure of about 45 lbs. per square inch, is turned on. The lead is thus thoroughly stirred, and as it cools crystallization takes place. Any crusts which form on the sides of the pan are pushed down into the molten lead, the steam being temporarily stopped.

After about an hour, two-thirds of the lead will have crystallized, and the steam valve is so arranged that when this occurs the contents of the pan offer so much resistance that the steam will no longer pass in. The taphole is then opened, and the liquid lead run out into the moulds. The fire under the crystallizing pan is replaced, and the crystals melted ready for another charge from one of the melting pans. It is needless to say that this lead must have the same content of silver as the melted crystals in the crystallizing pan.

The time for a complete operation will generally be about four hours.

A modification of the Luce-Rozan process has been introduced by Fredinnick, and is in operation at the Omaha Works of the American Smelting and Refining Company. In it there are twelve 50-ton pans, one for each crystallization, as in the Pattinson process, but each pan is supported by a hydraulic ram, so that it can be raised and the fluid lead run off from the crystals into the next pan. The pans are heated by gas, which burns inside a brick-lined jacket. The method has the advantage of being able to deal with a very much larger quantity of lead (more than twice the amount) in a given time than the Luce and Rozan process.

The Parkes Process.—This process is based on the following facts :—

1. That when zinc and lead are melted together and the molten mixture is allowed to cool slowly nearly complete separation of the two metals occurs, the zinc, on account of its slight solubility in lead, its higher melting point and lower specific gravity, solidifying first, forming an upper layer, which can be removed as a crust from the liquid lead.
2. The greater affinity of silver for zinc than for lead.
3. The greater affinity of gold for zinc than for lead.
4. The insolubility of the zinc-silver alloy in lead saturated with zinc.
5. The insolubility of the zinc-gold alloy in lead not saturated with zinc.

Blast-furnace or hard lead must be first softened, in the manner already described, in order that any copper, arsenic, or antimony present may be reduced to very small proportions. This is necessary, because copper consumes zinc, and if arsenic or antimony is present the silver can only be removed by many additions of zinc.

The operations to be performed in the Parkes process are :—

1. Softening of the argentiferous lead to remove copper, arsenic, and antimony.
2. "Zincing." The addition of zinc in two or three successive amounts, to remove the gold and silver from the lead.
3. Liquation of the zinc crusts, or now pressing them in a Howard press, to separate adherent lead.
4. Distillation of the liquated crusts, with the production of rich lead ready for cupellation, and metallic zinc.
5. Cupellation of the rich lead.
6. Refining the desilverized lead, in order to remove the zinc which is retained in it.

The plant required:—

1. One or more softening furnaces.
2. Two or more desilverizing or "zincing" pots or "kettles."
3. Two or more liquation pots, or a liquation furnace, or a Howard press.
4. Several retort furnaces for the distillation of the zinc crusts.
5. One or more reverberatory softening or refining furnaces for removing the zinc dissolved in the lead.
6. One or more "merchant" pots or kettles, from which the lead is cast into moulds.

The entire plant should, when possible, be so arranged that the lead from one operation can be tapped, or siphoned, into the pot or furnace in which the succeeding operation has to be carried out.

The kettles or pots are of cast iron. They resemble in form those for Pattinsonizing, and each is set over its own fire. In capacity they range from 30 to 60 tons. A kettle holding 30 tons is a common size, and its dimensions are 8 feet 10 inches in diameter and 3 feet 4 inches deep. Some of the largest kettles are elliptical, thus a 60-ton kettle would measure 10 feet 10 inches in length, 8 feet 9 inches in width, and 3 feet in depth.

Zincing.—The amount of zinc used necessarily varies with the amount of silver and gold in the lead. It varies, too, in different works, even for lead of the same richness in silver.

Lead containing 0·5 per cent. silver (163 ozs. 6 dwts. 16 grs. per ton) requires not more than about 2 per cent. zinc, but in usual practice less fresh zinc is added as the last crusts are used again.

The operation of zincing will be readily understood if we consider the working of a charge in a 40-ton pot of about 33 tons of lead from the softening furnace, containing 300 ozs. silver and 5 dwts. gold per ton. The pot is charged by running into it the lead from the softening furnace. The lead is skimmed or drossed, and then heated somewhat above the temperature required to melt zinc, which should not be less than 450° C., the melting point of zinc being 419° C. About 200 lbs. of zinc are then added to remove the gold. This is called the gold-zincing. The slabs of zinc are either simply placed in the lead, or are enclosed in a wrought-iron perforated box to which a handle is attached, and pushed to the bottom of the pot. Sometimes the zinc is melted and poured into the lead. When the zinc has melted the contents of the pot are thoroughly mixed by stirring with an iron paddle, or rarely by passing in dry steam. In almost all large works, however, the Howard mechanical stirrer is employed.

The Howard stirrer, which is shown in Fig. 83, consists of a horizontal screw propeller, revolving in a specially constructed frame. The frame carries a stout cover, which rests on the top of the pot, to exclude the air.

The propeller is driven by bevel gearing actuated by a small steam or compressed-air engine, or by an electric motor. The whole is hung from a traveller, which runs upon the same overhead rails used for the Howard press, to be described later.

The fire is then damped down and the lead allowed to cool gradually. The zinc after a time begins to solidify in the form of crusts. These are lifted up with a disc-shaped perforated iron skimmer, allowed to drain, and then transferred to a mould, or a liquation pot, or a Howard press is employed when liquation is not necessary.

The Howard press is shown in Figs. 84 and 85.[*] It consists of a cast-iron cylinder F with a perforated tilting bottom, and a screw press, which is worked by a motor B. The whole is fitted in a frame suspended from a traveller, so that it can be lowered into any pot of a series. It is operated as follows:—When the crusts are forming it is lowered into the pot, and as soon as it has reached the temperature of the lead, the crusts are pushed into the cylinder. When full it is raised by the motor against the toothed plunger C, to press out the fluid lead. The cylinder is then lowered and brought up against the plunger several times, the latter being slightly turned each time, so that the teeth enter the mass of crusts in different positions. The press is then removed from the pot, the bottom tilted, and the cake of crusts dropped out and broken up for retorting.

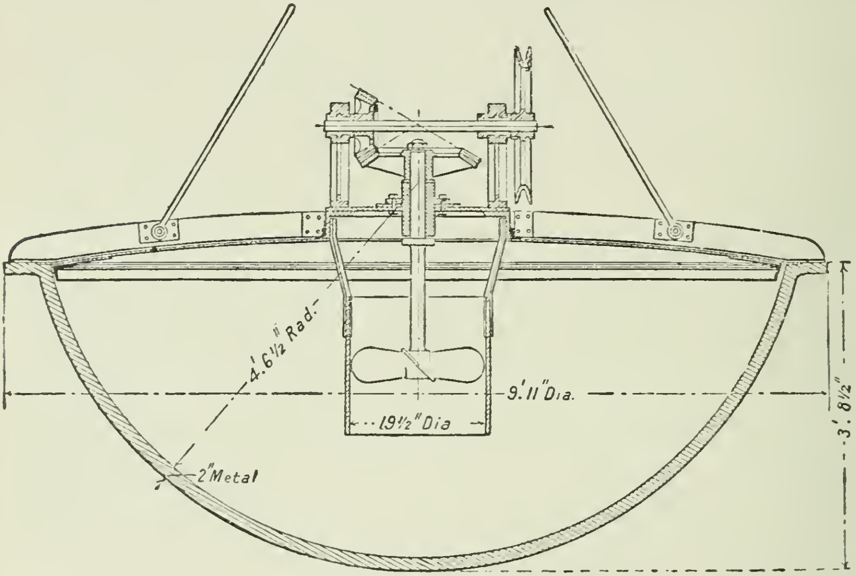

Fig. 83.—The Howard Stirrer.[†]

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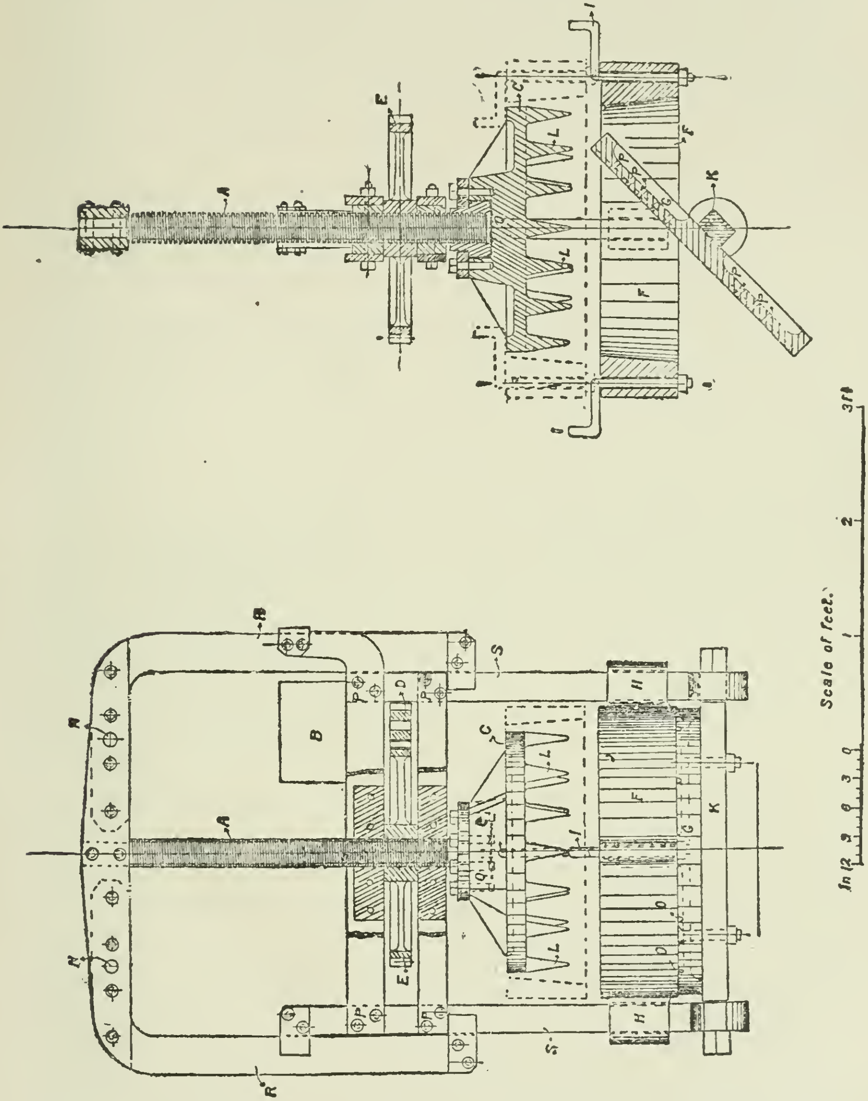
[*] Collins, *op. cit.*, p. 415.

[†] Collins, *op. cit.*, p. 403.

The crusts from this first zincing contain practically all the gold, nearly all the copper, with a little silver, and are kept separate from the subsequent crusts. They are generally too poor to be treated by themselves, and are therefore used for the first zincing of two other charges. They do not contain much silver, as the amount of zinc added was insufficient to saturate the lead with zinc, and until that occurs but little silver is removed from the lead. If the lead is rich in gold it cannot be removed by one zincing, so that

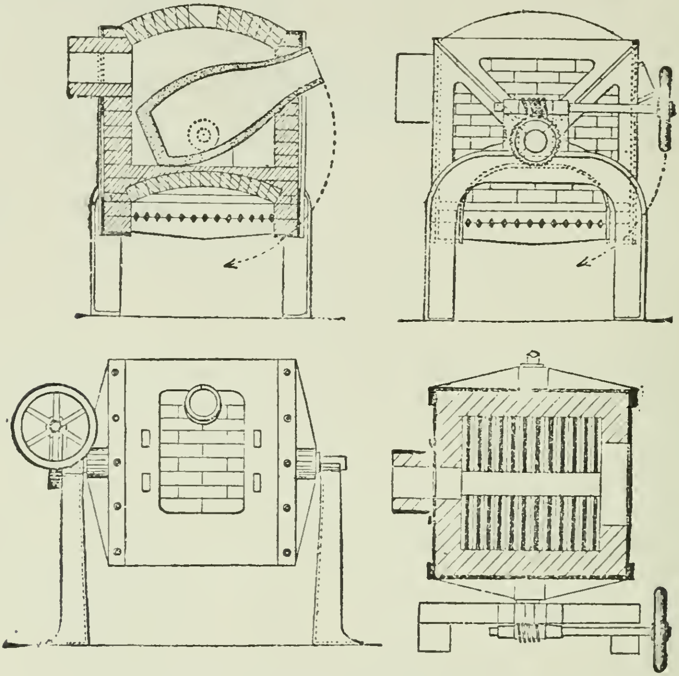


Figs. 84 and 85.—The Howard Press. (Collins, *op. cit.*, p. 415.)

it is often preferable to make only a silver crust which will contain the gold also. The lead is now again heated, about 650 to 750 lbs. of zinc are added, and the crusts which form on cooling are removed in the same way as the former crusts.

These crusts contain by far the greater part of the silver which was present, and the lead will then be left with only about 90 ozs. silver per ton.

Another 600 to 700 lbs. of zinc are added and removed as crusts in the same way. These crusts are used together with some fresh zinc for the second zincing—*i.e.*, the first desilverizing zincing of the next charge.



Figs. 86 to 89.—Faber du Faur Tilting Furnace.*

The time required for the operation will be about eighteen hours.

If the Howard press is not used the zinc crusts are liquated for the separation of the excess of lead with which they are mixed. This is accomplished by heating them to a little above the melting point of lead on the sloping hearth of a small reverberatory furnace, or in iron pans with conical or sloping bottoms, when the lead drains away. This lead is added to the next charge in the desilverizing pan. The zinc crusts are broken up whilst hot and distilled.

An excellent form of distillation furnace, which is largely used in the United States, and is being adopted in many works elsewhere, is the Faber du Faur tilting furnace, which is illustrated in Figs. 86 to 89.

It consists of an air furnace, set in an iron frame, suspended on trunnions, so that it can be tilted for pouring.

The retort in which the distillation takes place is of plumbago, and takes a charge of about 1,000 lbs. or more. A condenser of sheet iron lined with fire-clay, or an old retort, is fitted outside to receive the zinc. The fuel in the furnace shown is coke, but oil-firing has been introduced with advantage at many works. The zinc crusts before charging are broken to the size of nuts, and mixed with 1 to 2 per cent. of ground charcoal. After the first crusts charged have begun to melt, and have settled down, more are introduced until the retort has received its full charge. The condenser is then attached, and the distillation proceeds. The condensed zinc is tapped from time to time into moulds, and is set apart for use in subsequent zincing operations. When the distillation is completed the rich lead is poured out from the retorts into moulds by tilting the furnace.

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* Collins, *op. cit.*, p. 422.

The operation must be carefully conducted and violent ebullition avoided, or, as has been shown by Dewey,* from 28 ozs. to 604·5 ozs. of silver per ton may be carried over into the condensed zinc. If ebullition is avoided only slight amounts of silver are volatilized. He has further shown that the presence of lead in the crusts does not promote volatilization of the silver; on the contrary, it protects the silver from the " drag " of the volatile zinc.

The argentiferous lead left after distilling off the zinc is sent to the cupellation furnace. It will contain from 2,000 to 5,000 ozs. silver per ton.

The desilverized lead will contain about 0·6 to 0·7 per cent. zinc, and 4 to 6 dwts. silver per ton. It is transferred by means of a syphon to a reverberatory softening furnace similar to that already described (p. 227), in order that the zinc may be removed, and the lead made suitable for the market as soft lead.

An important innovation for the transference of lead is the introduction of centrifugal pumps instead of siphons. The depth of a pot or kettle is hence no longer limited to 40 inches, and their sizes can be greatly increased.

The operation for the removal of the zinc is a very simple one. The lead, which has been transferred from the desilverizing pot into the furnace, is heated to redness with free admission of air, a higher temperature being required than in the ordinary softening process. Two or three skimmings are usual, the lead being allowed to cool before each skimming and again strongly heated. The metal is then run into the " merchant " kettle, from which it is cast, as described on p. 229.

The time required for the process is from six to sixteen hours.

The American Smelting Co. carry out the removal of the zinc from the desilverized lead by pumping the lead in fine streams through a closed cylinder filled with chlorine. The zinc chloride formed during the later stages of the process contains much lead chloride and is used in a preliminary treatment of further batches of lead.

Comparison of the Pattinson with the Parkes Process.—The Pattinson process has the following advantages:—1. The appliances and the process itself are very simple. 2. Very pure lead is obtained. 3. Bismuth is removed, and can be obtained from the rich lead. 4. Specially suitable for fairly pure lead poor in silver.

Its disadvantages are:—1. Large cost of labour. 2. Large stock of lead to be kept on hand. 3. Requires great prolongation of the softening process for blast-furnace lead, and is less suitable for this lead than the Parkes process. 4. Not suitable for auriferous lead.

The advantages of the Parkes process are:—1. Much less labour required, and cost of treatment less. 2. Much less loss of lead and silver. 3. Extraction of gold.

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* *Eng. and Min. Journ.*, July, 1919.

4. Produces a richer lead for cupellation (2,000 to 5,000 ozs. silver per ton against Pattinson, 500 to 650 ozs.).
5. Less silver left in the market lead (4 to 6 dwts. against 9 to 10 dwts. in the Pattinson process).
6. Copper is removed.

At small mines, where the operations are limited in extent, it may be advisable to sell the argentiferous lead. At large mines, on the other hand, the lead should always be desilverized, and the products for sale should be pig lead and refined silver, as the profits will thereby be greatly increased.

The rich lead from the Pattinson process, which may contain 250 to 600 ozs. of silver per ton, or that from the Parkes process, which may contain as much as 2,000 to 5,000 ozs. of silver per ton, has now to be cupelled for the separation of the silver.

Cupellation.—The process of cupellation is carried out in two different types of furnace—viz., the English and the German. The chief characteristics of each type of furnace are as follows :—

The English Furnace.—(1) The hearth is movable, and the roof fixed.
(2) The lead is charged in continuously during the operation.
(3) The silver can be refined in it if necessary ; this, however, is not always advisable.
(4) The litharge is always more or less argentiferous.

The German Furnace.—(1) The roof is movable, and the hearth is fixed.
(2) All the lead is usually charged in at once.
(3) Crude silver only is produced in it.
(4) Fairly pure litharge is produced for sale.
(5) Yield of silver small in proportion to the size of the hearth.

The German furnace has been, wherever it was in use, almost entirely replaced by the English furnace, except in Germany itself.

The principle on which the operation of cupellation is based is as follows :—
When argentiferous lead is kept molten, at a proper temperature, and exposed to a blast of air, the lead is oxidized, forming litharge ; other metals, with a few exceptions, are also oxidized and dissolved in the litharge, whilst the silver and any gold which may be present are left unoxidized.

On a small scale, as in cupellation in assaying, the litharge with the dissolved oxides is absorbed by the cupel, but on a large scale this is impossible, and only a small portion is absorbed, whilst the remainder flows away and is collected. Nearly all the foreign metals are oxidized before the whole of the lead. Bismuth, however, remains with the silver until near the end of the operation, when it too is oxidized, and hence may be extracted, as at Freiburg, by keeping apart the litharge last formed.

The English Process.—The cupellation of the rich lead from the Pattinson or the Parkes process is accomplished by melting it in a large cupel called a "test," which forms the bottom of a small reverberatory furnace, and keeping it at a temperature exceeding the melting point of litharge whilst exposed to a blast of air. The litharge is run off as it forms until at last metallic silver alone remains.

The oxidation of the lead is effected partly by the action of the blast of air, and partly by the litharge which absorbs an excess of oxygen. The other metals present, except silver and gold, are also oxidized, and their oxides are dissolved by the litharge and pass off with it. A portion of the silver also enters the litharge, especially during the last stages of the operation. This litharge is put aside and the silver recovered from it.

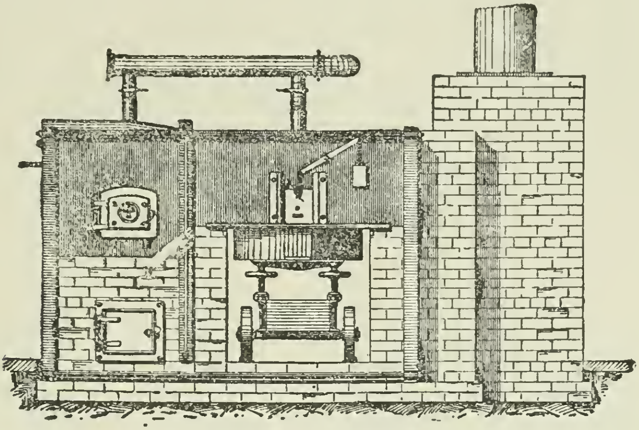

Fig. 90.—English Cupellation Furnace.*

English Cupellation Furnace.—The construction of this furnace has been somewhat modified in American practice, and although the original form is still found in some works, the former is in more extensive use. The two forms differ chiefly in the larger size of the test and the arrangements for supporting it. The furnace is a reverberatory one, with a fire-place very large in proportion to the hearth (Figs. 90 and 91). The large fire-place is necessary, as a temperature of nearly 1,000° C. has to be maintained in order to keep the litharge molten (melting point of litharge about 954° C.).

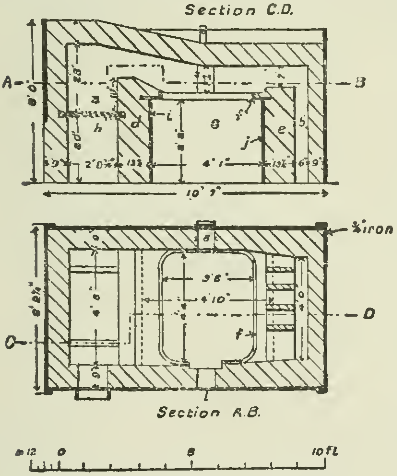

Fig. 91.—American Cupellation Furnace.†

The space below the hearth is quite open to admit the carriage which carries and supports the hearth or test. It is closed at the top by the compass ring, which is let into the brickwork, and by the test, which is fitted inside the compass ring when the furnace is at work. The flue leading from the furnace to the downtake is divided into four channels of different areas, so arranged that the flame is drawn more over the front of the test, where the litharge runs out, than over the back.

There are generally three openings or doors in the back of the furnace—

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* Collins, *op. cit.*, p. 438. † Collins, *op. cit.*, after Hofman, *Metallurgy of Lead*, p. 519

viz., one for the blast pipe, and two for feeding in the pigs of lead—but sometimes there is only one opening, which serves both for the blast pipe and for charging in the lead.

In the front side there is one door at the point where the litharge is discharged. The hearth or "test" was formerly always oval in shape, as in Fig. 92, but modern tests are generally made oblong, with rounded corners, because that form presents a larger surface for oxidation. The oval form consists of an iron ring with a bottom of a few cross-bars forming a frame, into which bone-ash or other material is rammed, the dimensions ranging from 3 feet 2 inches by 2 feet 1 inch to 4 feet by 2 feet 6 inches.

The dimensions of the oblong frames sometimes reach 4 feet 3 inches by 3 feet 5 inches, as in Fig. 93. At Port Pirie they are even larger, measuring 5 feet by 4 feet, their capacity when new being at least 1 ton. They are similar in construction to the oval frames, but are usually of cast iron.

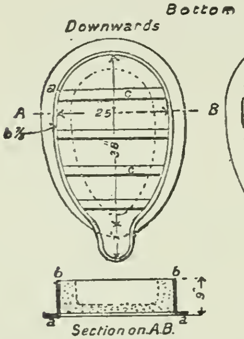

Fig. 92.— Oval Test Rings.*

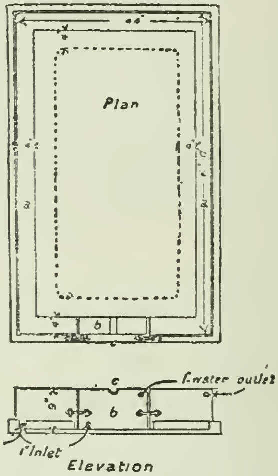

Fig. 93.—Rectangular Water-Jacketed Test.†

Materials for the Construction of the Test.—Bone-ash has now been largely given up, and in its place the following materials are used :—

(*a*) A mixture of ground limestone and fire-clay.
(*b*) ,, ,, ,, and Portland cement
(*c*) ,, 5 parts Portland cement and 1 part of sand.
(*d*) ,, ground limestone, fire-clay, magnesia, and cement.
(*e*) Portland cement alone.

Whatever material is used, it is moistened with water and firmly tamped into the iron frame, the working cavity being formed during the tamping. At Port Pirie the cavity is formed by means of an oiled wooden mould, which is pressed down into the material by heavy weights.

The test is sometimes water-jacketed by making the test ring hollow so that water may be circulated in it.

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* Collins, *op. cit.*, p. 440.

† Collins, *op. cit.*, p. 442, after Hofman, *Metallurgy of Lead*, p. 523.

In some cases an iron pipe is embedded in the material of the test for the same purpose. The life of the test is thus prolonged. In the furnace in Fig. 90 the test is supported on a small carriage carrying four screw-jacks (Fig. 94). In another form of carriage there are two screw-jacks at the back and a hand-screw in front, so that by lowering the front screw the test can be inclined and its contents poured out (Fig. 95). In some works the Lynch test-support is in use. By its means the test can not only be lowered in front, but also at either side, if one side is being more corroded than the other.

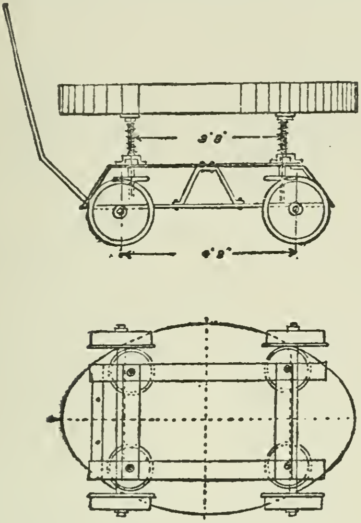

Fig. 94.—Test Carriage with Oval Ring (Fraser & Chalmers).

The Blast.—This is delivered through a flat nozzle about 4 inches by ½ inch. It was formerly produced by means of a steam jet, but now a Roots' blower or fan is commonly employed. The blast pressure ranges from 5 to 12 ozs. per square inch.

The Process.—The test is gradually heated to redness, and then the lead is charged in in the form of pigs or bars, at first through the openings both at the front and back of the furnace, afterwards through the back only. The lead gradually melts and fills the cavity, and as soon as it attains a cherry-red heat, the melting point of litharge, the blast is turned on. The litharge formed runs out through a notch at the breast of the test, and is received in a conical iron pot below. Pigs of lead are gradually pushed into the furnace, so that they may melt down at such a rate that the lead in the test may be kept always at the same level. The flow of litharge must also be regulated, so that about one-half of the surface of the lead remains covered, in order

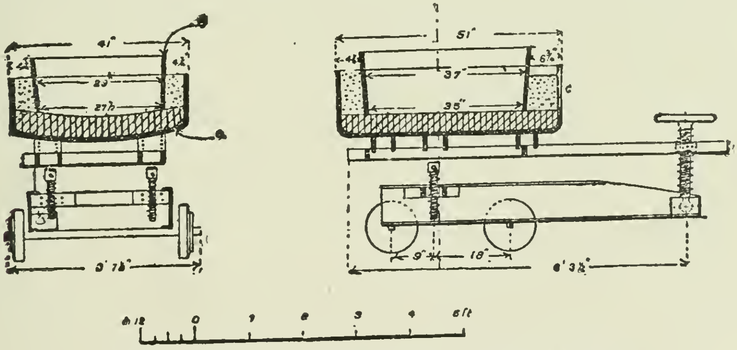

Fig. 95.—Rectangular Brick Test with Tilting Carriage.*

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* Collins, *op. cit.*, p. 441

to avoid undue loss of lead by volatilization. When the charge in the test has been concentrated to the required degree, say to bullion containing 50 to 60 or 70 per cent. silver, the blast is stopped, and the contents of the test are laded into moulds, or poured if the test-support is a tilting one. The working of a new charge is then begun.

The rich bullion is taken to a similar furnace, the "finishing" furnace, where the cupellation is carried further until silver of 997½ or higher in fineness is obtained. This is usually laded into moulds holding about 1,000 ozs.

The German Process—The Furnace.—There are two varieties—viz., the older form with a circular hearth and the modern with an elliptical hearth.

In both cases the working bottom is of marl, marl and clay, or of a mixture of limestone with clay, damped and tamped on a bottom of red brick. In the furnaces with circular hearths the roof is of the form of an inverted saucer, and consists of fire-tiles set in an iron frame, which can be raised and moved by means of a crane. The hearth is about 9 or 10 feet in diameter. The fire-place is at one side, and the flue immediately opposite it. The tuyeres, of which there are two, enter at one side nearer the fire-place than the flue. The litharge notch is nearly opposite, but still nearer the fire-place.

In the modern oblong furnace with elliptical hearth the roof is of similar construction, but is flat, and is lifted and moved by an overhead traveller. Otherwise, the furnace is of the ordinary reverberatory type. The dimensions of the working hearth are about 11 feet by 8 feet.

The Process.—The roof is lowered, and luted with clay to the furnace After the hearth has been warmed, the pigs of lead are charged in through the working doors, generally upon a bed of straw. The process may be divided into the following stages :—

(1) The fire is made up and the lead melted down slowly, the blast turned on, and the dross skimmed off when most of the copper is removed.

(2) After the skimming, litharge containing arsenic and antimony rapidly forms, and is drawn off through the litharge notch.

(3) Next pure litharge begins to flow.

(4) Finally, the litharge during the later stages contains silver, and is set aside to be smelted.

(5) At the end of the operation the silver brightens, when two pieces of bar iron are placed in the cake, before solidification, to serve as handles. The hearth is cooled with water, the roof raised, and the cake of silver lifted out by a crane.

(6) The crude silver (*blicksilber*), 950 to 980 fine, is refined in another furnace with a smaller hearth, or sometimes by melting it in a crucible with silver sulphate, which will remove lead and bismuth, but not copper.

A modification of the above method of cupellation has been adopted at some works in Germany, by which it approximates somewhat to the English process. A full charge of the rich lead is placed in the furnace, and as it is oxidized additions of fresh lead are gradually made up to as much as 50 to 60 tons, and the oxidation is only continued until the bath contains 80 per cent. of silver. The concentrated alloy is cupelled and refined on a smaller hearth.

Comparison of the English and German Methods—The English Method.—

1. Best for the rich lead from the Parkes process.
2. Small cost of labour.
3. Small cost of hearth and hearth material.
4. Smaller quantity of old hearths to be resmelted.

It has one disadvantage—viz., that less pure litharge, practically none, is produced for the market.

The German Method.—1. More suitable than the English method for Pattinson lead low in silver, and for very impure lead.

2. Smaller consumption of fuel.

3. Production of a comparatively pure litharge for sale. This is its chief recommendation, and the main reason for its use.

Its disadvantages are :—

1. The furnace has to be cooled and the cake of silver pulled out, hence much labour and loss of time.

2. Much hearth material has to be smelted.

Typical modern examples of the desilverization of lead are afforded by the procedure at the following plants :—

Desilverizing Lead at Port Pirie.*—" The bullion is first heated in two sets of ' softening ' reverberatories ; in the first set copper is removed, and in the second set, where a higher temperature is used, the antimony is skimmed off. The softened lead then passes to ' zincing ' pans, of which there are five sets of two pans each.

" Four of these sets are in constant use, and the fifth is held in reserve. In each set of two, one is working a later stage of the operations than the other. The pans each hold from 35 to 40 tons of bullion. In pouring the lead into the pan a thick dross forms on the surface ; this is skimmed off when the pan is full, and returned to the reverberatory copper-separating furnaces. The first addition of zinc is made with the object of removing the gold. The addition consists of 200 lbs. of spelter and 50 lbs. of zinc recovered from the retorts. After melting and stirring for half an hour with a mechanical stirrer practically all the gold and some of the silver enter the zinc. The pan is then allowed to cool until the alloy hardens on the rim. The alloy is removed by means of shallow perforated iron ladles, with the assistance of wooden rakes, and thrown into moulds.

" The bullion on going into the pan assays about 50 ozs. silver with variable but small quantities of gold, and after the first ' zincing ' 45 ozs. silver and only a trace of gold. If the gold content after the first zincing should be over 2 grains of gold per ton, another ' first ' zincing will be made with 120 lbs. of spelter.

" The charge is now prepared for a second zincing for the removal of part of the silver. It is kept hot for two hours, and then 700 to 800 lbs. of silver-zinc alloy, obtained from the third zincing of the previous charge, is added to the pan, and the contents stirred for half an hour. The pan is then allowed to cool, and the floating alloy is removed and separated from the lead through a pneumatically operated press. The alloy is dropped upon an iron cone, in order to split it into convenient sizes for retorting. The lead remaining in the pan contains about 25 ozs. silver, and after 2½ hours heating a third zincing is done by the addition of 300 lbs. of retort zinc and 275 lbs. of spelter. After stirring and cooling, the alloy is skimmed off with perforated skimmers and wooden rakes, thrown into moulds, and then stacked by the pan for addition in the second zincing of the next charge. The lead now contains, as a rule, less than ½ oz. silver per ton, but if more than this a further zincing is required, 75 lbs. of spelter being added if the content is from 2 to 5 ozs., the final content then being only ⅓ oz. per ton.

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* *Min. Mag.*, vol iii., pp. 225-6. Abstract from the *Australian Mining Standard*, July 27, 1910.

"With regard to the gold skimming from the first zincing, the content varies from ½ to 8 ozs. gold and 70 to 160 ozs. silver per ton. It is charged into a reverberatory, known as the gold alloy furnace, and melted with litharge from the cupels used subsequently. Part of the zinc is here volatilized, and part goes into slag. The bullion produced assays 150 to 240 ozs. silver, and from ½ to 1½ ozs. gold. This is charged by hand into a 'special' zincing pan, where it is melted and treated with 300 lbs. of spelter, and the resulting alloy removed by a press. If the assay of the remaining charge is over 2 grains of gold per ton, the charge is treated to another zincing reaction; if the resulting alloy is rich enough it is mixed with the alloy from the previous zincing; if not, it is added to the charge in the first special zincing pan. The resulting alloy from these special pans, called the 'special gold alloy,' is retorted, some of the zinc recovered, and 'special gold bullion' produced. The special gold alloy assays from 100 to 350 ozs. silver and 1 to 10 ozs. gold per ton, and the special gold bullion varies from 800 to 1,500 ozs. silver and 100 to 300 ozs. gold per ton. The special gold bullion is concentrated in a cupellation furnace, and then goes to the parting plant.

"As regards the recovery of the silver, the pressed alloy from the second zincing is retorted, and the bullion produced is first concentrated in a cupellation furnace until it reaches a richness of 16,000 ozs. per ton, and it is then finished in another furnace."

A typical example of English cupellation is afforded by the practice at Port Pirie. The tests of the concentration furnaces are cooled by a 1-inch water pipe round each. The lead which contains on an average 3,000 ozs. silver per ton is cupelled at the rate of about 66 cwts. in twenty-four hours, being concentrated to about 50 per cent. silver, as stated above, when it is laded into moulds and sent to the finishing furnace. The litharge contains about 30 ozs. silver per ton and is smelted. The test of the finishing furnace has a capacity of about ½ ton. The silver produced is about 997½ fine. A small amount of gold goes into the silver bullion, which usually assays from 1 to 2 ozs. gold to the ton. The litharge contains 200 ozs. silver per ton, and goes to the softening furnace to assist in the oxidation of the antimony.

The Sulphide Corporation's Lead Refinery at Cockle Creek,* New South Wales.—The installation is in two units in parallel, each unit consisting of one 50-ton copper-drossing kettle, one 46-ton antimony softener, two 44-ton desilverizing pans, one 40-ton refiner, one 38-ton market kettle, one moulding ring; and common to both sets, one small furnace for working up skimmings and drosses, one antimony dross furnace, one gas producer for retort-furnace, one four-bottle regenerative gas-fired retort-furnace, two single bottle oil-fired tilting retort furnaces, three concentrating cupellation furnaces, two finishing cupellation furnaces, electrolytic parting plant, gold and silver melting furnaces.

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* The *Min. Mag.*, July, 1919. Abstract of Paper by R. E. Cowles, read before the Australian Institute of Mining Engineers.

The base bullion, after being drossed and moulded (25 bars per ton) in the smelting department, is run on trucks to the copper-drossing kettles. The bars are charged into the kettle, melted at a low temperature, and the copper dross skimmed. After its removal the metal is transferred to the antimony softener by means of an electrically-driven centrifugal pump, The antimony softener is of the usual reverberatory type, water-jacketed, and lined with magnesite bricks at the litharge level ; the end jacket is centrally channelled, the channel leading into a removable inclined spout, carrying the litharge into portable slag pots. After charging, the furnace is strongly fired, in an oxidizing atmosphere, the resulting litharge being constantly run off at the channel, carrying with it the antimony and arsenic. Towards the end of the operation, the furnace is allowed to cool and the litharge is skimmed by hand.

The time required for the operation is 8 to 12 hours. After the removal of the antimony and arsenic the metal is tapped into one of the desilverizing pans, and the gold and silver separated by the Parkes process. The spelter is added in cakes and stirred in by means of a Howard stirrer. The zinc alloy pressed, in the Howard press, goes direct to the retorts. The desilverized lead is then siphoned to the refinery furnace of the usual reverberatory-jacketed type, and the zinc and any remaining antimony are removed as a dross by skimming. The refined lead then passes by gravity to the market kettle, from which it is siphoned into a pot and runner, and moulded in a semi-circular rake of 1 cwt. moulds. The pressed silver-zinc alloy from the desilverizing kettles is charged in 12-cwt. lots to the inclined bottles of the gas-fired retort furnace, the zinc distilled and condensed, and the bullion laded into moulds. The two tilting retort furnaces are a special feature of the plant. They are fired with oil from the Mond gas plant. A charge of 10 cwts. of alloy is finished each shift. When ready, the molten metal is poured into moulds by tilting the furnace. The retorted bullion, assaying 2,000 to 2,500 ozs. Ag per ton, passes to the concentrating cupellation furnace, where it is worked up to concentrated bullion containing approximately 16,000 ozs. silver plus gold per ton. The metal is laded into moulds and transferred to the finishing cupellation furnace. The bullion obtained is cast into rectangular anodes about ¼ inch thick, weighing approximately 100 ozs., and the gold and silver separated in the electrolytic parting plant.

Desilverization of Lead at the Perth Amboy Plant of the American Smelting and Refining Company, Raritan Bay, U.S.*—The working up of Mexican raw lead is carried on as follows :—

From each bar a sample is cut from above and below by means of a punch entering half-way into the bar.

For refining the lead there are four reverberatory furnaces of 60 tons capacity, with hearths 17 feet 9 inches by 12 feet 6 inches, a mean depth of 14 inches, and a grate area of 2 feet 6 inches by 6 feet ; in addition to these there is a furnace of 80 tons capacity, with a hearth 19 feet 7½ inches by 9 feet 6 inches, a mean depth of 18 inches, and a grate area of 3 feet by 6 feet.

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* *Eng. and Min. Journ.*, January, 1906.

For desilverizing the softened lead there are five kettles, each of 60 tons capacity, 10 feet 3 inches diameter, and 39 inches depth. The zinc is stirred in with a Howard mechanical stirrer, and the zinc scum is pressed dry in a Howard press, which gives a very dry scum. The latter is then, while still warm, readily hammered into pieces for the retorts.

The desilverized lead is refined in five reverberatory furnaces, of which four take a charge of 50 tons each, and one of 65 tons. The production of desilverized lead is 5,000 to 5,500 tons a month. The distillation of the zinc crusts is carried out in eighteen oil-fired Faber du Faur tilting furnaces. Each retort receives a charge of 1,200 lbs. of broken-up crust and a little charcoal. The distillation lasts six to seven hours. Fifty gallons of petroleum residues are consumed per charge. The oil is blown into the furnace with a compressed-air atomizer. After withdrawing the condenser, which runs on a travelling support, the argentiferous lead is poured directly from the tilted retort into an English cupel furnace. Seven such furnaces (magnesia-lined, with movable test) are in use, of which each works up 4·5 to 5 tons of retort metal in twenty-four hours. The furnaces are water-jacketed. The blast is introduced by the aid of a jet of steam. Three tons of coal are used per twenty-four hours.

The doré bars are cast into anodes for electrolytic parting by the Moebius process (p. 367).

Electrolytic Refining of Lead.—The electrolytic refining of metallic lead is carried out successfully by means of the Betts process, in which a solution of lead fluosilicate is used as the electrolyte.

Lead fluosilicate is extremely soluble in water, and the solution has not only a high conductivity, but is free from secondary decomposition in the vats, there being no polarization from the formation of lead peroxide on the anodes.

The process is carried out at the works of the United States Metals Refining Company at East Chicago, Ind., and at a number of other works. Gold, silver, and bismuth are recovered, and an exceedingly pure lead is obtained.

The first-named works has a daily capacity of 100 metric tons. Electrolysis is carried out in a solution containing 5 grammes of lead and 11 to 12 grammes SiF_6 per 100 c.c.; after it has been in use for some time, the solution contains 0·2 to 0·3 per cent. of free hydrofluoric acid. In addition, 400 to 500 grammes of gelatine are used for every ton of lead deposited to ensure a smooth, compact, and adherent deposit.

Electrolysis is carried out at a temperature of from 30° to 35° C. With the electrodes separated 1¾ inches apart, and a current density of 15 ampères per square foot, the E.M.F. for a vat is 0·22 volt, to which should be added 0·10 volt for other resistances. If the electrolyte becomes richer in lead the voltage is increased. The current efficiency reaches to 85 to 90 per cent.

The anodes measure 3 feet by 2 feet, and are 1 inch in thickness. They consist of base bullion, and are cast, in iron moulds, with lugs for suspension in the vats. The cathodes are of pure lead, 2 feet 8 inches long, 2 feet 10 inches wide, and about $\frac{1}{16}$ inch thick. The vats used for the electrolysis are of wood coated on the inside with asphalt. Each vat contains 22 to 28 anodes and 23 to 29 cathodes. The cathodes remain in the bath four to five days, the anodes twice as long; hence a double set of cathodes is necessary. The electrolyte is circulated from vat to vat, the vats being arranged in cascade. It is necessary to avoid, as far as possible, exposure of the electrolyte to the air, or antimony is liable to be oxidized and dissolved and deposited on the cathodes, hence the fall from vat to vat is made as small as permissible.

The 33 per cent. hydrofluosilicic acid used in preparing the electrolyte is made at the works themselves, at a cost of about 1½d. per kilo. The anode scrap averages about 29 per cent., and is utilized in casting other anodes. A large part of the anodes is converted into sludge, which is brushed off from time to time. The sludge, which contains notably the silver and the gold, is washed, filter-pressed, and dried. It is then melted in a reverberatory furnace with a basic lining. During this operation there are produced auriferous and argentiferous lead containing the bismuth, a slag consisting of lead oxide and antimony oxide, and sometimes an argentiferous copper matte. The great bulk of the arsenic present is volatilized.

The chief advantages of the process are small loss of lead and large recovery of the other metals present. Further, according to Betts, it can be worked economically for the treatment of as small a quantity as 1 ton of lead per day. When the process has been properly conducted the Cu, As, Sb, and Fe in the lead produced will not exceed the following percentages:—Cu, 0·0003 to 0·0009; As, nil to 0·0008; Sb, 0·0003 to 0·001; and Fe, nil to 0·001.

The silver present will be only 4 to 7 grammes per ton, and bismuth will be absent.

The electrolytic plant at Trail (1913) is described by J. F. Miller in the *Journal of the Canadian Mining Institute.* The base lead bullion produced in the blast furnaces contains about 97 per cent. Pb, the remaining 3 per cent. consisting of Au, Ag, Sb, As, Cu, Zn, and traces of other metals. This lead is cast into anodes weighing about 400 lbs. each.

The vats are 7 feet 4 inches long, 2 feet 6 inches wide, 3 feet 8 inches deep, and hold 20 anodes placed 4⅛ inches between centres. There are 240 vats, with a daily capacity of 65 tons of pure lead.

The cathodes are sheets of pure lead placed between the anodes. The electrolyte contains 12 per cent. of hydrofluosilicic acid and 6 per cent. of lead fluosilicate. To prevent the deposition of soft, spongy lead and short-circuiting, glue is added to the electrolyte in the proportion of ½ to 1 lb. per ton of lead produced. The electrolyte is circulated through the vats at the rate of 35 cubic feet per hour. Two set of cathodes are used, the first being renewed after five days, and the second when the anodes are reduced to about 15 per cent. of their original weight. The anode scrap is melted and cast into anodes. The anode mud which contains Au, Ag, Cu, Sb, and As is washed, dried, melted, and cast into bars to be parted with sulphuric acid. The gold, silver, and copper are recovered. The plant is arranged for the recovery of the antimony also, but it is not in operation. The refined lead contains Pb, 99·9938; Zn, 0·0005; Ag, 0·0013; Cu, 0·00075; Fe, 0·00075; Sn, 0·0001; Sb, 0·0028 per cent.

GOLD.

Physical Properties.—Gold is the only metal which has a yellow colour when in mass and in a state of purity. The colour is greatly modified by impurities, silver lowering the tint, while copper heightens it. When finely divided it may assume violet, ruby, purple, dark brown, or black colour.

Malleability and Ductility.—In malleability and ductility it exceeds all other metals. Leaves of gold not more than $\frac{1}{300,000}$ of an inch in thickness can be obtained by beating, and a single grain can be drawn into a wire 500 feet in length. Less than 0·1 per cent. of lead, bismuth or tellurium renders gold brittle, owing to the distribution of Au_2Pb, Bi or $AuTe_3$ between the grains.

Hardness.—It is softer than silver, but harder than tin.

Tenacity.—Pure gold has a tenacity of 7 tons per square inch, with an elongation of 30·8 per cent.

Specific Gravity.—Its specific gravity when cast varies from 19·29 to 19·37.

Action of Heat.—The melting point of gold is approximately 1,063° C.—that is, just below that of copper, and about 100° higher than that of silver.

Volatilization of Gold.—The conclusions to be drawn from a recent important research by Sir T. K. Rose at the Royal Mint, London, on the volatilization of gold as a whole may be stated as follows :—[*]

1. True volatilization of gold is so small as to be negligible at the temperatures of industrial melting furnaces, say 1,000° to 1,300°. It is difficult to measure with accuracy the infinitesimal amounts volatilized at these temperatures.

2. It is probable that the nature of the atmosphere, provided that it is maintained unchanged, has no effect on volatilization. Even in a strong draught, the amount volatilized remains exceedingly small.

3. Certain gold alloys when molten take up oxygen from atmospheres containing it, and will afterwards spirt or effervesce in a reducing atmosphere until the oxygen has been removed. Similarly, hydrogen, and in a less degree carbon monoxide, is occluded by such molten alloys, and the metal then spirts in an oxidizing atmosphere. In spirting, showers of globules of the alloys of all sizes are thrown up, and the smaller ones, especially those of less than 0·001 mm. in diameter, are carried away by any draught, how-

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[*] Sir T. Kirke Rose, "The Volatilization of Gold," *Trans. Inst. Min. and Met.*, 1919, vol. xxviii., p. 135.

ever slight, and are difficult to recover. They can be collected by such a filter as cotton wool.

4. The action is observable in all the alloys of gold with silver or copper. Even parted gold containing one part per 1,000 of silver is affected, though to a far less degree than coinage alloys, gold-silver parting alloys and similar materials. Fine silver and its alloys with copper also spirt freely.

5. It is this action which causes the unrecovered losses in melting such alloys in crucibles, without a cover of slag.

In ordinary melting furnaces the total amount of loss probably seldom exceeds 0·1 per thousand in melting a charge of 1,200 ozs.

The rate of loss during melting does not depend entirely on the temperature. The passage of a current of air over the surface of the molten metal increases the amount, so that if the lid of the crucible is removed for any purpose the loss is increased. The presence of volatile impurities in bullion also causes increased loss.

Lead only very slightly increases the volatility of gold. Copper and zinc have a more marked effect, while 5 per cent. of antimony or mercury will cause a loss of 2 parts per thousand at 1,245° C.

" The loss of gold on melting its copper alloy is the common experience of mints. The melting loss is usually about 0·2 to 0·25 per 1,000, and after taking account of the amounts recovered from the ground-up crucibles, ashes, floor sweepings, and furnace bricks, it still amounts to 0·1 or 0·15 per 1,000." *

According to Rose's experiments at the Royal Mint, tellurium does not cause volatilisation of gold below 1,100° C. Hence the losses incurred in roasting telluride ores are not due to volatilization.

Electrical Conductivity.—Its electrical conductivity is 76·7, that of silver being 100.

Atomic Weight.—197·2, taking that of oxygen as 16.

Effect of Foreign Substances on Gold.—Even when present in minute quantities, Pb, Bi, Cd, Sb, As, and Sn produce brittleness. Tellurium also has the same effect. Osmium and iridium as osmiridium do not alloy with the gold, but remain as hard grains in the mass, and are found chiefly at the bottom of ingots.

Chemical Properties.—The chief solvents of gold in industrial use are *aqua regia*, solutions of chlorine, and potassium cyanide. It is also soluble in any mixture producing nascent chlorine, as, for example, solutions containing mixtures of (1) nitrates, chlorides, and acid sulphates ; (2) chlorides and some sulphates—*e.g.*, ferric sulphate ; (3) hydrochloric acid and nitrates, peroxides, such as permanganates, or chlorates ; (4) bleaching powder and acids.† Gold is soluble in solutions of bromine, or of mixtures producing bromine, and in boiling concentrated solutions of ferric chloride. Iodine dissolves gold only if it is nascent, or if dissolved in an iodide, or in ether or alcohol. It is also soluble in solutions of the thiosulphates (hyposulphites) of calcium, sodium, potassium, and magnesium, in the presence of an oxidizing agent.

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* Rose, *Metallurgy of Gold*, p. 9.

† Rose, *Gold*, p.18.

Sulphuric acid, hydrochloric acid, and nitric acid separately have but little action on the metal. It is not perceptibly attacked by alkalies. If nitric and sulphuric acids are present together, gold is dissolved.

It is also attacked by alkaline sulphides producing gold sulphide, which is dissolved (see p. 352).

The chief precipitants of gold in industrial use for obtaining the metal from these solutions are :—

1. *Ferrous sulphate* on a large scale from solutions of gold chloride at chlorination mills, and in the *aqua regia* parting process. The reaction is :—

$$2AuCl_3 + 6FeSO_4 = Au_2 + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$

2. *Sulphuretted hydrogen* also at chlorination mills, and in the von Patera process for silver ores when gold is present.

The precipitate produced in either cold or hot solutions appears, as a rule, not to be a definite sulphide, but a mixture of the three gold sulphides with free sulphur and metallic gold (Rose).

3. *Sulphurous Acid* (sulphur dioxide).—Chiefly in use in laboratories in the preparation of pure gold from chloride solutions, and not on a large scale as precipitation is slow until the solution is saturated with the gas.

$$2AuCl_3 + 3SO_2 + 6H_2O = Au_2 + 6HCl + 3H_2SO_4.$$

4. *Charcoal.*—In use formerly, on the largest scale, at the chlorination works at Mt. Morgan (Queensland) (p. 276). The reaction which occurs has not been fully investigated.

It has also been used at some small cyanide plants (see p. 332).

5. *Zinc.*—In extensive use in the form of extremely thin shavings or dust in cyanide plants for precipitating the gold from cyanide solutions, the reaction being :—

$$2KAuCy_2 + Zn = K_2ZnCy_4 + 2Au.$$

6. *Aluminium.*—In the form of powder aluminium is also in use for the precipitation of gold in the cyanide process.

Gold is also separated from cyanide solutions by electro-deposition (see p. 367).

Gold Chlorides.—There are two chlorides, AuCl and $AuCl_3$. Only $AuCl_3$ auric chloride, or gold trichloride is of metallurgical importance. Gold trichloride is very soluble in water. In the air it is readily decomposed by heat, the decomposition being complete at 220° to 230° C. with the formation of gold and chlorine. Even at 100° C. it is decomposed, but very slowly. It is also decomposed by light, whether dry or in solution, but not when free hydrochloric acid is present.

The volatilization of gold trichloride, which is of importance in the roasting of ores with salt, has been found by Rose to begin at about 180° C. and to reach a maximum at about 250° C. It then falls off gradually up to 800° C., when it again increases. Between 500 and 800 (very dull red to red heat) the volatilization is small.

Solutions of gold trichloride are decomposed and the gold precipitated by many reducing agents, as, for example, sulphur dioxide, oxalic acid, ferrous sulphate, ferrous chloride, phosphorus, charcoal, and most organic substances and metals, the decomposition in every case being hastened by heating. They are reduced very rapidly by zinc and iron, and more slowly by lead, gold being precipitated. Sulphuretted hydrogen completely precipitates the gold as sulphide, both from acid and neutral solutions.

The chief precipitants used on a large scale in a works have already been mentioned. In the preparation of pure gold in laboratories sulphur dioxide and sometimes oxalic acid are the reagents employed.

Ferrous sulphate is frequently used to detect the presence of gold in solution as chloride. Two test-tubes or Nessler tubes are placed side by side on a sheet of white paper. One is nearly filled with the solution to be tested, the other with water, and a few drops of a solution of ferrous sulphate are added to each. On looking down the tubes a brown colouration, due to finely divided gold in suspension, will be seen in the tube containing the chloride solution. In this way the presence of only $\frac{1}{720,000}$ part of gold in the solution (1 dwt. per ton of water), or even less can be detected.

A still more delicate test for the presence of minute quantities of gold in solution as chloride is afforded by the reaction of a mixture of $SnCl_2$ and $SnCl_4$ in solution with $AuCl_3$, by which a precipitate of purple of Cassius is produced.

The solution containing $AuCl_3$ is heated to boiling and poured suddenly into a large beaker containing 5 to 10 c.c. of a saturated solution of the stannous chloride, when a precipitate is at once produced which will be coloured, or tinted purplish-red or blackish-purple, even if the solution contains as little as 1 part of gold in 5,000,000 parts of water ($3\frac{1}{2}$ grains per ton). By this test Dr. Rose has detected the presence of 1 part of gold in 00,000,000 parts of water (1 grain in 6 tons).

Gold cyanides will be considered under the " Cyanide Process," p. 336.

The hyposulphites of gold are of importance to the metallurgist in connection with the extraction of the metal from silver ores by the process of leaching with sodium or calcium hyposulphites, and by the Russell process.

Alloys of Gold.—Although gold alloys with most metals, only a few of the alloys are of practical use either in the arts or manufactures. The most important are those which gold forms with mercury, with copper, and with silver.

Gold and mercury form a complete series of alloys which are termed amalgams. These vary from the liquid to the solid state according to the relative proportion of gold and mercury.

Gold, however, unites with mercury to form a white solid amalgam containing about 32·75 per cent. of gold.

When excess of mercury is present, as in the amalgamation of gold ores in mills, this amalgam will be suspended as particles in it, and can be separated by straining it through chamois leather.

The amalgam thus obtained will always contain some mercury, and will, moreover, be very variable in composition, as it always contains particles of gold which have only been partly penetrated by mercury. The gold will range from about 25 to 50 per cent., being highest when the ores contain the metal in coarse grains.

When the amalgam is heated by distillation in retorts, as at mills, the mercury is volatilised, condensed, and collected, but usually about 1·0 or 1·5 per cent. is left in the gold, and is only expelled when the gold is melted.

Gold and Silver.—Gold and silver unite in all proportions, forming homogeneous solid solutions which, as the proportion of silver is increased, become lighter in colour until, when between 60 and 70 per cent. is present, they are quite white.

They are all malleable and ductile.

When the alloys contain not less than 60 per cent. of silver, the silver is almost completely dissolved out by nitric or by sulphuric acid; but if less is present the silver is only partly removed.

Aqua regia attacks these alloys, but its action is soon stopped by the coating of AgCl which forms on the surface of the metal.

The alloys are used in jewellery, as, for example, "green gold," containing 25 per cent. of silver, but triple alloys of gold, silver, and copper are most common.

Alloys of gold with various proportions of silver, from 35 to 86 per cent., have been largely used in Japan for the old gold coinages and for gold jewellery, a perfect gold surface being obtained by dissolving out the silver from the upper layers of the alloy by pickling processes.

A native pale yellow alloy of gold and silver *electrum* was the metal used for the earliest known coins, which were made by Gyges in Lydia in the seventh century B.C., and was also much used for ornaments by the Greeks and Romans. It contained from 15 to 35 per cent. of silver.

Gold and Copper.—Gold alloys with copper in all proportions, giving alloys which are harder, less malleable, and ductile, but more elastic than the unalloyed metal.

Segregation takes place to such a slight extent on solidification when the metals are of ordinary purity that it may be disregarded. The presence of lead and bismuth, however, will cause segregation.

Gold-copper alloys containing excess of copper are acted on by nitric acid and by sulphuric acid in a similar manner to gold-silver alloys, the copper being dissolved and the gold left behind.

The gold-copper alloys are in extensive use for jewellery.

The standard gold in England consists of 916·6 parts of gold and 83·4 parts of copper, and is that adopted for the gold coinage.

The gold coins of Portugal, Turkey, India, Brazil, Chile, and Peru are also of this composition.

In France, America, and most other countries, the standard consists of 900 parts of gold and 100 parts of copper. The Egyptian standard, however, has a fineness of 875, while the Austrian ducat is 986$\frac{1}{9}$, and that of Holland 983. The English and the French standards are the best for coinage, the latter resisting wear more than the former.

For gold wares in England the standards recognized by law are those containing 22, 18, 15, 12, and 9 parts of gold in 24 parts. These are designated by the term "carat," an alloy of 22 parts of gold and 2 parts of copper being called 22 carat gold, and so on, and all can be stamped after being assayed at the Goldsmith's Hall, or other Government offices in the country, with the number indicating its fineness, a mark denoting the office, and a date mark.

The best jewellery is of 18 carat, but 22 carat is used for wedding rings.

Gold alloys with iron, and the more readily if the molten gold is at a high temperature, hence the metal should not be stirred, when molten, with an iron rod.

Segregation in Gold Alloys.—The alloys in which segregation is of special importance to metallurgists are those of gold-silver-lead-zinc produced in cyanide mills.

This has been investigated by Edward Matthey,* with the following results:—

One such ingot, which weighed about 120 ozs., when assayed gave 662 parts of gold per thousand at one of the bottom corners, and only 439 parts at the top.

Another, which weighed 400 ozs., and contained 16·4 per cent. of lead and 9·5 per cent. of zinc, yielded 614·0 parts of gold per thousand and 75·8 parts of silver by actually separating the whole of the precious metals, its true value being, therefore, £1,028. While the value deduced from the average of fourteen assays made on it (gold 576·0, silver 90·0) would have been only £965. Seven dip assays made on this ingot varied from 562 to 622 parts of gold per thousand. The segregation in other ingots was even more remarkable.

In experiments on alloys of gold and zinc, he found that gold tends to segregate towards the centre of the masses, but only in a slight degree, the centre of a sphere, 3 inches in diameter, of an alloy containing gold 90, zinc 10, being only about 1 to 2½ parts per thousand richer than the outside. In alloys of gold and lead the segregation was much greater, the centre of a 3-inch sphere being 29 parts per thousand richer than the outside when 30 per cent. of lead is present.

A still greater segregation takes place when lead and zinc are present together, thus in an alloy containing 15 per cent. of lead and 15 per cent. of zinc, the sphere contained 657 parts of gold at the top, 785 in the centre, and 790 at the bottom, gravity thus playing a part.

If, however, silver is present, or is added in such an amount that it is not less than about two-thirds of the quantity of zinc and lead taken together, segregation does not take place. An alloy containing approximately gold 55, zinc 7, lead 18, silver 20 was found to be practically homogeneous.

Matthey † has also investigated the segregation which occurs in gold ingots containing members of the platinum group. When such gold is cooled from a state of fusion, an alloy rich in the more fusible element (gold) falls out first, driving the less fusible constituent to the centre. Thus the assay of an outside cut of such an ingot gives a result too high in gold, sometimes by several per cent.

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* *Proc. Roy. Soc.*, vol. lx. (1896), p. 21.

† *Proc. Roy. Soc.*, vol. li. (1892), p. 447; and *Phil. Trans. Roy. Soc.*, vol. clxxxiii. (1892), A, pp. 629-652.

The behaviour of osmium and iridium has been already discussed (p. 249).

OCCURRENCE OF GOLD.

Gold occurs very widely distributed in nature, and almost always in the metallic state, containing a varying amount of silver, with smaller proportions of copper and other metals. It usually occurs in veins and alluvial deposits, but there is a very considerable distribution of the metal, in minute invisible particles, in rock formations without any connection with veins.

A very rich deposit occurs in a bed of lignite in Japan; it is also found in coal at the Cambrian coal field of Wyoming.

All copper ores contain it, generally only in minute quantities, but the author has found as much as 26½ ozs. per ton in copper from one of the Northern mines in Japan.

Gold Ores.—Gold is extracted on the largest scale from veins or lodes, from alluvial deposits called "placers," and from rock masses, as the "banket," as the conglomerates of the Transvaal are termed.

Vein Gold.—In veins gold occurs in granular, arborescent, dendritic, wire-like, and irregular forms, but rarely in crystals, traversing and intimately penetrating the quartz, which commonly forms the gangue. It is also found in thin laminæ, which when pyrites is present frequently form films on the crystalline faces. Usually, however, it is intimately disseminated in invisible particles through the substance of the mineral.

"*Placer*" *or Alluvial Gold.*—The sands, gravels, and detritus of ancient streams which have been derived from the disintegration of auriferous veins or rocks are termed "placers."

The gold in these occurs chiefly in small scales, rounded grains, and pellets, and is called "gold dust."

Larger masses, generally more or less rounded and mammilated, of various sizes up to over 2,000 ozs. also occur. They are termed "nuggets."

The minerals which most commonly occur in association with gold are magnetite, iron pyrites, zinc blende, copper pyrites, arsenical pyrites, stibnite, platinum, and irid-osmine. The above sulphides occasionally carry gold, notably iron pyrites which is frequently auriferous, and also arsenical pyrites.

Other minerals are calcite, garnets, ilmenite, zircon, gypsum, etc.

Gold Tellurides.—The following are the tellurides of chief importance:—

Calaverite.—A bronze-yellow mineral. Localities—West Australia, California, and Colorado. Composition at Kalgoorlie—Au 40·6 to 42, Ag 0·8 to 2·2; the remainder Te.

Sylvanite.—Graphic tellurium, so called, because the arrangement of the crystals resembles written characters.

White and brass-yellow in colour. Localities—As above, and Transylvania. Composition at Kalgoorlie—Au 25·5 to 26·1, Ag 11·3 to 15·0 per cent.

In the American localities it contains Au 5·6 to 7·6, and Ag 32·3 to 34·2 per cent.

Petzite.—Localities as last, with the addition of Chili and Utah.

It is a telluride of silver in which some of the silver is replaced by gold. At Kalgoorlie it contains about 25 per cent. of gold.

Nagyagite, or foliated tellurium. Foliated like graphite. Locality—Transylvania.

Contains gold 9 to 13 per cent., and lead 54 per cent.

Kalgoorlite.—Iron-black in colour. Localities—Kalgoorlie, Colorado, and Transylvania. Composition at Kalgoorlie—Au 21·0 to 23·9, Ag 29·3 to 31·9, Hg 4·7 to 10·0 per cent. The proportion of mercury is very variable.

Composition of Native Gold.—Native gold always contains silver, the amounts varying from 1 to 380 parts per thousand.

The fineness of the gold hence ranges from 610·0 (in the Andes) to 999·0 (Cripple Creek) per thousand.

Placer gold in	California formerly assayed	883·6	in fineness.
„	Japan ranges from	620 to 904	in fineness.
„	Korea „	764 to 873	„
„	Australia averages	950	„
Vein gold in	Japan ranges from	566 to 926	„

Copper is also present in small amounts. Palladium (in Brazil), rhodium (in Mexico), bismuth (in Victoria), mercury (in New Granada), and iron are occasionally present.

EXTRACTION OF GOLD FROM ORES.

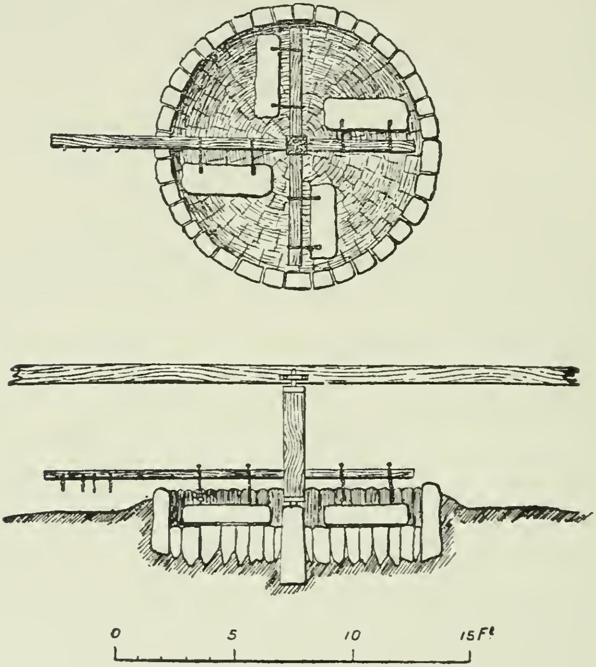
Gold which occurs in placers is extracted by washing in more or less simple appliances, such as the pan, cradle, long-tom, and sluices, and by dredging, but the operations carried on belong rather to the miner than to the metallurgist, and hence do not come within the scope of this book. See Rose, *Metallurgy of Gold*, pp. 99-144.

Gold Milling.—As gold, which occurs in veins or rocks, is generally more or less intimately interwoven with or disseminated through the matrix, it can only be separated by first breaking, crushing, and pulverizing the material, and subsequently or at the same time subjecting it to the action of various reagents.

The breaking is effected by various forms of rock breakers, as the Blake or Dodge, and their modifications, or gyratory crushers, and the crushing and pulverization, with or without amalgamation, by stamps, the Huntington mill, Chilian mills, ball mills, grinding and amalgamating pans, and the tube mill, also by rolls for dry work. The chief reagents employed are mercury, potassium cyanide, and chlorine.

One of the earliest crushing machines which was largely in use in Mexico, chiefly in preparing silver ores for the patio process, is the arrastra. It is now almost obsolete, but deserves mention here on account of its power of saving gold, its simplicity, low cost, and its great value in prospecting a claim before modern milling machinery is erected. Its effective action is due to the fineness with which it grinds, the long time during which the ore and mercury are in contact, and the clean surfaces produced on the particles of gold by rubbing between the stones.

A typical arrastra is shown in Figs. 96 and 97, from which it will be seen that it consists of a pavement of stone surrounded by a circular wall of stones. The grinding is effected by huge stones, weighing from 6 to 12 cwts., which act as mullers, and are hung from the cross-arms of a vertical shaft, usually revolved by mule-power. It is worked as follows:—The ore is charged in, and after being ground fairly fine, water is added to make it rather a stiff pulp. The mercury for amalgamation is then sprinkled over the surface. When the ore is sufficiently ground the pulp is diluted with water and run out. Time, 6 to 12 hours.



Figs. 96 and 97.—Arrastra (Plan and Section).*

Most of the amalgam remains in the arrastra, and is obtained at the clean-up. The amalgam in the pulp is separated in large dolly-tubs. The crushing and amalgamation of gold ores in the stamp battery will now be considered.

The Stamp Battery.—This is in practically universal use in gold milling.

Whenever an ore contains free gold in appreciable quantity it can be extracted by amalgamation in the stamp battery, except in a few exceptional cases.

About 1 to 5 per cent. clean cubical iron pyrites does not affect the amalgamation, but with 20 per cent., or much less if marcasite, galena, zinc blende, or compounds of As and Sb are present, amalgamation is retarded or prevented altogether.

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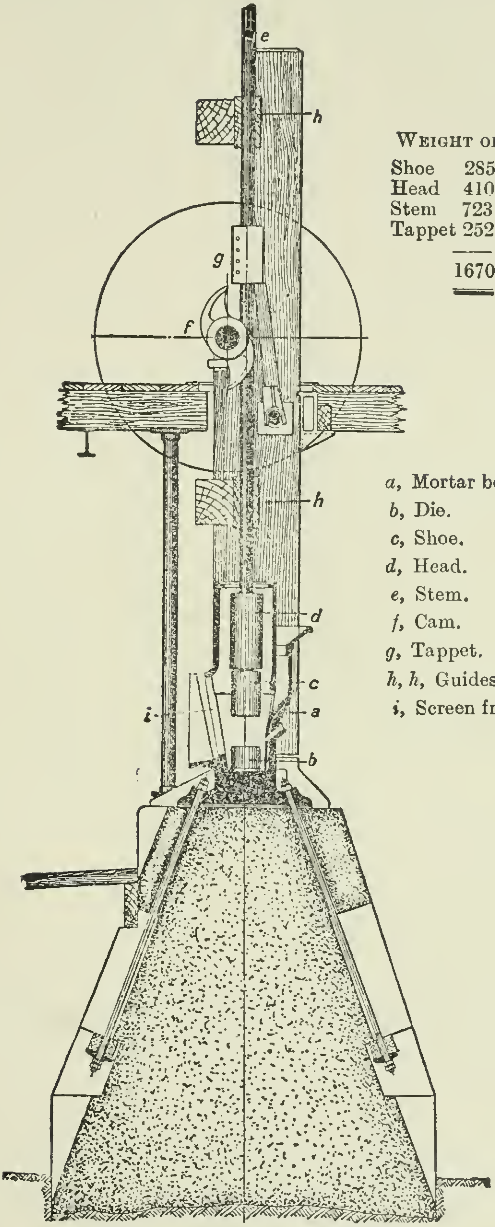
* Collins, *Silver*, p. 40.



Weight of Stamp (New).

Shoe	285 lb.	=	17·066%
Head	410 ,,	=	24·551%
Stem	723 ,,	=	43·293%
Tappet	252 ,,	=	15·090%
	1670 ,,	=	100·000%

a, Mortar box.
b, Die.
c, Shoe.
d, Head.
e, Stem.
f, Cam.
g, Tappet.
h, *h*, Guides.
i, Screen frame

Fig. 98.—Heavy Gravitation Stamp.

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* Caldecott, *Trans. Inst. Min. and Met.*, vol. xix , p. 64.

When the battery is employed alone as an amalgamator, slow running stamps, with a high drop, wide mortar, fine-screen apertures, and high discharge, are needed to retain the pulp within the mortar for a sufficient length of time to amalgamate as much as possible of the gold.

Ores containing coarse free gold are best suited for the process.

Ores containing very finely divided gold can be treated, but then they must be kept for a long time in the mortar, so that when coarse and fine gold are present together in an ore it is best treated by amalgamating first to extract the coarse gold, and then to recover the fine gold by subjecting the tailing to the cyanide process.

The stamps employed almost everywhere are the Californian gravitation stamps, and, as this term gravitation denotes, they act by their falling weight. They are arranged in sets of five, in a strong wooden frame, which carries the cam shaft and the guides in which the stamps work.

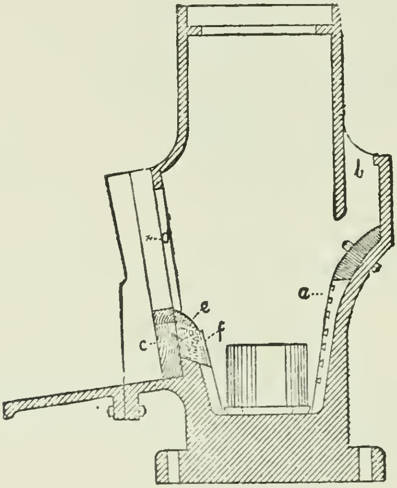

Fig. 99.—Mortar Box.*

A mortar box or mortar, containing five dies or anvils, on which the ore is pounded, serves for each set of five stamps.

In Fig. 98 † is illustrated a modern heavy gravitation stamp, as in use in the Simmer Deep Jupiter joint mill.

The Mortar Box.—This is a heavy iron casting of the form shown in Figs. 98 and 99, having in front an opening, into which the screens are fitted, and at the back a feed shoot, through which the broken ore is delivered.

In some forms of mortars screens are fitted both at the back and the front, so that there is a double discharge.

The mortar box rests on a firm foundation, formerly of timber, but now in the Transvaal and elsewhere of concrete, as in Fig. 98. The screen frames are fitted with screens of wire cloth of brass or steel, or of Russian sheet iron or mild steel perforated with holes or slots. The size of the apertures in these varies according to the work required of the stamp; if for fine crushing they may be 20 or 40 mesh, but since the installation of tube mills and grinding pans, especially the former, the function of the stamp battery is to crush the ore coarsely, the fine grinding being performed in one or other of the appliances to be described later, hence screens with apertures of even 3 mesh (9 holes per square inch) are used.

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* Rose, *Gold*, p. 161. † Caldecott, *Trans. Inst. Min. and Met.*, vol. xix., p. 64.

There are many ores from which it is desirable to remove as much of their gold as is practicable at as early a stage of their treatment as possible, and amalgamation in the mortar box was formerly used for this purpose.

In these cases, amalgamated copper plates were fitted to one or more of the sides, and in addition mercury in small quantities was charged in from time to time.

The vertical distance between the top of the die and the upper edge of the bottom of the screen frame is termed the height of discharge, and it is of the first importance that this should be kept as uniform as possible. This is effected by chock blocks of varying heights placed beneath the screen, and so by changing them the screen can be lowered as the dies wear. A shallow or a deep discharge is also determined by the height of the chock blocks. A shallow discharge promotes rapid crushing and speedy exit of the pulp from the mortar. A high discharge has the opposite effect.

The Dies.—These are cylindrical castings of the same diameter as the shoes, with a square or rectangular foot plate with bevelled corners. They are usually 7 inches in height.

The Stamp.—The stamp consists of the following parts:—The stem head, shoe, and tappet.

The total weight of a stamp has undergone great changes during recent years, the tendency being always to increase it, as it had become obvious that to crush more rock a heavier blow must be struck. Compensating weights have become common, but in the most up-to-date mills the whole stamp has been made heavier. Thus, while formerly 900-lb. stamps were the almost universal maximum, we have now on the Rand stamps weighing 1,670 lbs., as shown in Fig. 98, and at the City Deep 2,000 lbs. (see also p. 265).

The stems are made of wrought iron or soft steel turned perfectly true, and tapered at each end to fit the head, so that if one end breaks the other can be used.

The head or boss, which is of cast steel, has two conical sockets, one to receive the stem and the other the shank of the shoe.

It is usually 15 to 24 inches long, but on the Rand the length ranges from 20 inches to 4 feet.

The shoes are of the same diameter as the head, 9½ inches in the case of the 1,750-lb. stamps, and 8 to 9 inches in stamps of less weight. They are cast with a shank, which is fitted into the socket in the end of the head with the aid of dry wooden wedges.

The length of the butt is from 9 to 18 inches.

Both shoes and dies are made of cast iron, cast steel, forged steel, manganese steel, and chrome steel.

The tappets are made of tough cast iron or steel, and have a flange at both ends, so that they are reversible. They are keyed to the stem by one, two, or three gibs and keys, according to the weight of the stamp.

The stems of the stamps work in an upper and lower series of guides, which consist of wooden or iron boxes bolted to the two cross beams, by which the battery posts are connected. The stamps are raised by cams, the double cam (Fig. 100) of cast steel being in almost universal use. Each cam is fitted to the cam shaft, which should be of steel, by means of two keys. There are three types of cam shaft on the Rand, carrying respectively 5, 10, and 15 cams.

The cam shaft rests in bearings attached to the battery posts, and is driven by a pulley, preferably built up of wood.

The function of the cam is to raise the stamp to the maximum height, and at the same time to rotate it; this it effects by engaging with the tappet.

When the maximum height has been reached, the cam leaves the tappet and the stamp drops, but no grinding action results.

The rotation tends merely to uniform wear of the shoe and die.

The amount of drop, and the order in which the stamps shall fall, are of the first importance. The first is regulated by the position of the tappet and the curve of the cam, and varies from 4 to 18 inches.

The number of drops per minute in gravitation stamps necessarily varies with the height; with a 9-inch drop the maximum practical limit is 95 drops per minute, and with an 8-inch drop 100 to 108.

The order in which the stamps shall fall is so arranged that the ore may be evenly distributed over the dies, and as the end stamps have less expulsive effect on the pulp than the others, they are given a slightly longer drop.

A common order in America is 1, 4, 2, 5, 3, while on the Rand it is 1, 3, 5, 2, 4. Good results have been obtained in Brazil with the order 1, 5, 2, 4, 3. A good supply of *clean* water is essential. A water pipe is led along the front of the battery, from which there branches off two smaller pipes for each mortar box, by which the water is discharged about opposite the centres of the second and fourth stamps.

An elevation and section of a modern stamp battery are shown in Figs. 100 and 101.

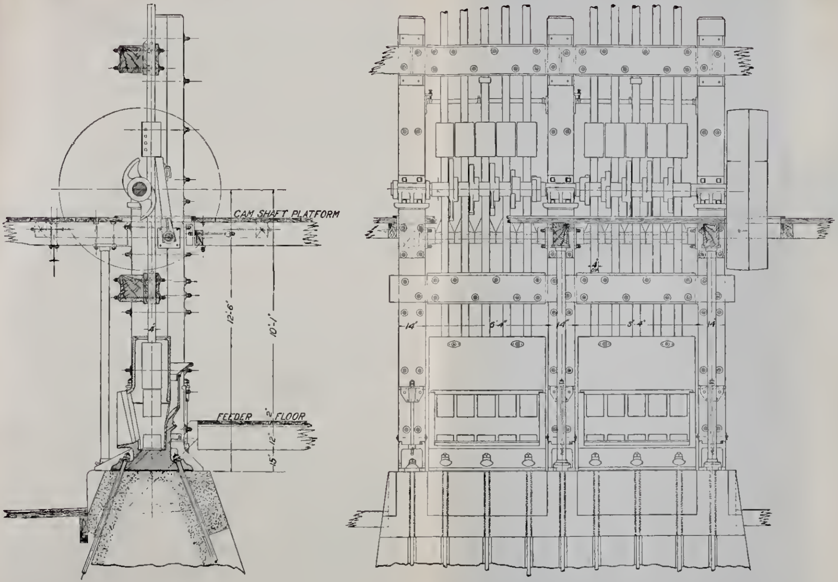
The Amalgamating Table.—This is set immediately in front of the mortar, but independently of the battery frame to exempt it from the jarring of the stamps. Its width should not be less than that of the discharge. Length from 6 to 15 feet, or sometimes 20 feet. If the gold is coarse a short table will suffice; if fine a long table is necessary.

The table is covered with copper plates, $\frac{1}{8}$ inch thick, which fit it exactly, and are secured in position by means of cleats or wedges. The inclination of the plates will vary between $\frac{1}{2}$ inch and $2\frac{1}{2}$ inches to the foot.

For tube-mill plates on the Rand the standard grade is $2\frac{1}{16}$ inches.

The copper should be the purest possible. At some mills the table is continuous, the copper plates fitting each other accurately, occasionally being brazed together. In others the table is broken up into steps, with a drop of 2 to 3 inches at each step. In the latter cases a 15-foot table would be made of five plates, each 3 feet long, with a drop of 2 inches between each.

The copper plates have to be amalgamated. They are first annealed. The plate is then thoroughly cleaned with fine sand and emery paper until quite bright, and any grease removed with a solution of soda. Mercury is then well rubbed in with the aid of sal-ammoniac or potassium cyanide. Before use, silver amalgam, or more rarely gold amalgam, is rubbed in; the plates then begin at once to catch gold.


CAM SHAFT PLATFORM
FEEDER FLOOR
12'-6"
10'-1"
2"
12"
15"
4"
14"
5'-4"
14"
5'-4"
14"

Figs. 100 and 101.—Stamp Battery (Section and Front Elevation). (*Rand Metallurgical Practice*, vol. i., Fig. 15.)

Electro-silvered plates are also largely in use; they are superior to copper plates, as they catch gold well from the beginning, and are easily kept clean.

Plates of Muntz metal (copper 60 per cent., zinc 40 per cent.) are also in use. These also catch gold well from the beginning, but the amalgam adheres in only a thin layer, so that they have to be cleaned frequently, but the cleaning is easily done by means of rubber only, as the amalgam does not adhere to them so obstinately as to copper plates.

In amalgamating new Muntz metal plates,* the following are the steps to be taken:—Rub the surface of the new plate with fine, clean sand to get it mechanically clean, then wash it with a weak solution (1 to 6) of sulphuric acid to make it chemically clean. Then start to rub in a little mercury, rub in one place "until it bites"—that is, the plate becomes amalgamated. Give a circular movement to the flannel or mop. Once started the amalgamation spreads in ever-widening circles.

When at work the plates are dressed about every four hours, being washed clean and rubbed with a hard brush or a rubber squeegee, or piece of rubber belting, sometimes with the aid of potassium cyanide; mercury is added, if necessary, and some amalgam is removed. The water supply must be such that the pulp flows in ripples slowly and steadily down the plates without sand settling anywhere upon them.

No part of the plates should be allowed to become dry, or dry particles of gold or amalgam may be floated away.

The times of dressing are, however, regulated by the richness of the ore. Great care is necessary in the amount of mercury used; both in the amalgamation of the plates and the subsequent dressings, just sufficient should be applied to keep their surfaces in a pasty condition.

At the bottom of the last copper plate it is advisable to place a mercury trap to catch any mercury or amalgam which may be washed off the plates.

Mercury and Amalgam Traps.—The pulp on passing over the lower edge of the amalgamated plate falls into a transverse trough variously arranged, so that any mercury or amalgam carried over will collect at the bottom, while the pulp overflows.

The stamp mill, however, at cyanide plants is now simply a "crushing" machine, and it has been questioned whether its work with ¼-inch mesh could not be done equally well by rolls or Chilian mills.

The stamp duty (or tonnage crushed per stamp in 24 hours), which in the days of the 900-lb. stamp did not exceed 3 tons, has grown to an average of 8½ tons for the whole Rand, and recent experiments have shown that, by crushing to an aperture of 0·284 inch and by introducing an elimination screen to "by-pass" the fine material from the rock breakers direct to the tube mills, it can be raised to as much as 26 tons per stamp.†

The researches of Mr. Caldecott, and other members of the Mines Trials Committee, have shown that the maximum diameter permissible for the battery feed is 1¾ inches, and that tube mills are most efficient when fed with ore discharged through a 9-mesh battery screen, having apertures of 0·27 inch, or, say, ¼ inch. The effective range of the stamp mill is, therefore, from 1¾ inches to ¼ inch.

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* Rickard, *Stamp Milling of Gold Ores*, p. 182.

† E. H. Johnston, *Journ. Chem. Met. and Min. Soc., S.A.*, vol. xi., 1910, p. 168.

As a result, at cyanide plants stamps are no longer employed for fine crushing, and amalgamation in the mortar boxes has been completely abolished. Further, even such plate amalgamation as took place in front of the stamp mills has, in many cases, been done away with.

When amalgamated plates are used they are placed after the tube mills (see p. 294).

The following is an outline of the treatment to which an ordinary gold ore in a quartz gangue is subjected in a modern gold mill (Fig. 102) * :—

1. The ore from the mine is tipped upon a grizzly, an inclined plane of bars leading to the floor of the rock breakers. The bars are set at such a distance apart that what goes through passes to the bin from which the stamps are fed.

The ore is broken in the rock breakers to about 2-inch cubes, according to Caldecott $1\frac{3}{4}$ inches, and goes to the same bin.

2. It is then fed into the mortar box of the stamp battery by an automatic feeder, a stream of water being directed towards the back of the box. By the fall of the stamps the ore is pulverized, and splashed up with the water against the screens, when the particles which are sufficiently fine pass through them out of the box.

3. The pulp which passes through the screens falls upon the amalgamated copper or Muntz metal plates, which catch the particles of gold.

4. The tailing is sometimes led by launders to classifiers, by which it is separated into sand and slime, or it goes to the tube-mill plant to be slimed, in each case for treatment by the cyanide plant. If it contains pyrites, it is led to Wilfley or Frue or other vanners, by which the pyrites is separated. The pyrites after separation is treated as described (p. 352), or sold to smelters, or formerly to chlorination plants when these were available. Sometimes the tailing was run over blankets, hides, or riffles in sluices, by which some gold and pyrites were caught, and this practice is still occasionally followed at the smaller mines.

5. The gold amalgam which accumulates on the amalgamated plates is wiped or scraped off from time to time. It is placed in a bag of chamois leather or canvas, the excess of mercury squeezed out, and the residue heated in an iron retort to distil off the remaining mercury.

6. The retorted bullion is then melted in plumbago crucibles when no fluxes are required, otherwise in clay or clay-lined crucibles with sodium carbonate, borax, etc., and cast into ingots.

The Clean-up.—This may take place twice a month, but there can be no rule, as it is determined by the richness of the ore. The mortar and dies are cleaned and scraped. The amalgam on the plates is carefully removed by rubber and iron scrapers, after which the plates are redressed. It is usually mixed with sand, pyrites, fragments of iron, etc., and has to be treated in the clean-up pan or revolving iron barrel before being retorted.

The clean-up pan is an iron pan, 3 to 5 feet in diameter, with revolving arms carrying shoes of wood or iron, or a continuous wooden muller, by means of which the amalgam is ground with fresh mercury and water (see "Silver," p. 384). The impurities rise to the surface and are removed.

The barrel in use on the Rand is a cast-iron cylinder, 4 feet long and 2 feet in diameter internally, mounted on trunnions. The dirty amalgam

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* Rose, *Metallurgy of Gold*, p. 177.

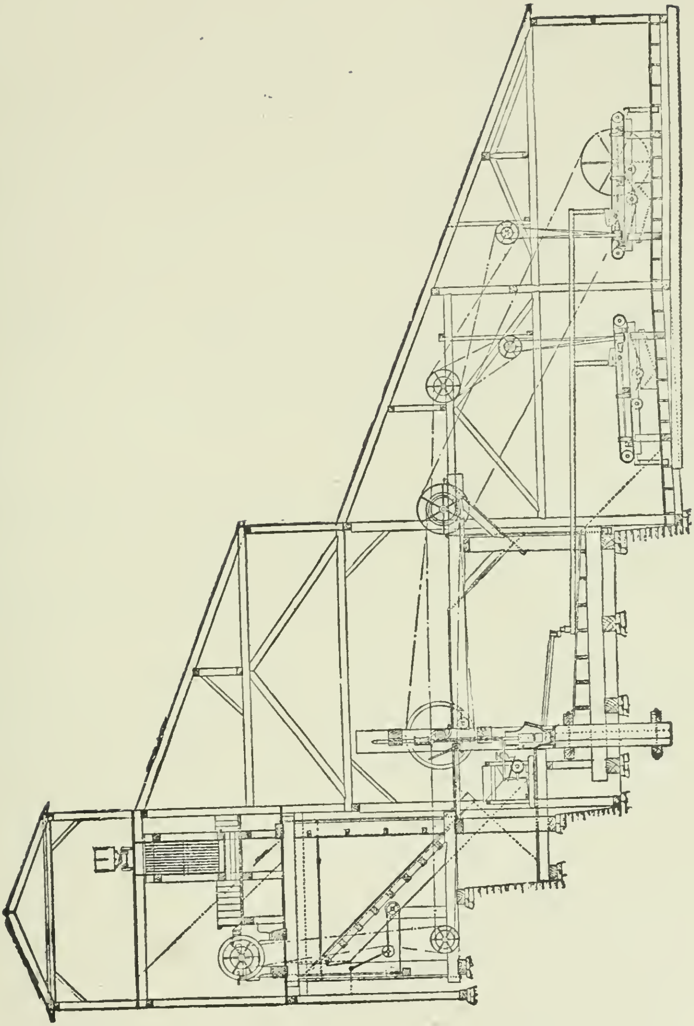

Fig. 102.—General Arrangement of Machinery in Stamp Mill.

is revolved in it together with iron balls, or pieces of broken stamp stems, and with sufficient mercury to give a fluid amalgam, and water to form a thin pulp. Time, about two hours. The contents of the barrel are then emptied into a shallow pan or *batea*, in which the amalgam is thoroughly washed.

The amalgam is then squeezed through canvas, and will contain approximately 30 to 45 per cent. of gold.

In large mills it is retorted in the cylindrical iron retort described under "Silver," p. 395; but in small mills a pot shaped iron retort is employed, a condensing tube cooled with water, like a Liebig condenser, being attached to condense the mercury. The amalgam is charged in, in the form of cakes or balls, the adhesion of the retorted metal to the iron being prevented by first white-washing the inside of the retort, or by placing inside three or four thicknesses of paper.

The metal after retorting is melted and cast into ingots, as described above.

Losses in Stamp-Mill Amalgamation.—The loss of mercury is very variable, ranging from $\frac{1}{4}$ to 1 oz. per ton of ore treated. It is chiefly due to "flouring" and "sickening." Mercury is said to be "floured" when it is in excessively finely divided particles resembling flour, which will not unite or take up gold or adhere to the amalgamated plates. It is caused by excessive stamping, being greatest in batteries with deep discharge, owing to the lengthened pounding. Mercury is said to be sickened when it is in similar fine globules, but which are coated with some substance which prevents them from coalescing. Talc, manganese oxide, galena, arsenical pyrites, stibnite, and grease all tend to produce sickening. Impure mercury containing base metals, especially lead, is readily sickened.

Floured and sickened mercury is readily lost through passing away in the tailing. The chief remedies in use in mills to prevent loss of mercury from the above causes are :—

1. Grease and oil should be kept out of the battery.
2. Sodium amalgam may be used to revivify sickened mercury, but has no effect if antimony sulphide is present.
3. The mercury should be cleaned by covering it with dilute nitric acid (acid 1 part and water 3 parts) and stirring it from time to time, or blowing air through it.
4. If very impure it should be treated as in 3, and then be distilled with lime and iron filings, or with sodium or potassium nitrate, or sodium peroxide.

Loss of Gold.—The chief losses of gold are due to the following causes :—

1. Loss of gold in floured mercury containing the metal.
2. Mechanical losses of amalgam.
3. Coarse particles of the ore containing gold.
4. "Float" gold—*i.e.*, finely divided gold.
5. So-called "Rusty" gold, not of common occurrence. It resists amalgamation, owing to its being covered with a film of some neutral substance.
6. Loss in pyrites and tellurides, subsequently recovered by other processes.
7. Loss in the tailing.

The above losses may be prevented or minimized by :—

1. Keeping the mercury clean and active.
2. The addition of the mercury in proper quantities, so that the amalgam is not too " dry " or fine particles may be washed away, and so that it does not accumulate as drops on the plates.
3. The use of mercury traps.
4. Finer crushing if the coarse particles contain gold.
5. The use of drops between the amalgamated plates, if " float " gold is being produced.
6. The loss in the tailing may be reduced to a minimum by treating it by the cyanide process.

Other Machines for Crushing and Amalgamating.—*Pneumatic stamps*, in which the stem is attached to a piston working against air in a cylinder ; *spring stamps*, in which the stamp is raised against powerful springs ; and *steam stamps*, driven by a steam cylinder above each stamp, are not generally employed for the milling of gold ores.

The Nissen Stamp (Fig. 103).*—Each stamp has its own mortar box (Fig. 103*a*). This is cylindrical, and the screen extends half round the mortar. The screen is, therefore, of large area, 3¾ to 4 square feet, it is at right angles to the splash, both features tending to promote effective discharge.

The entire crushing zone is protected from wear by liners of manganese steel.

The same number of parts per stamp make up the falling weight, as are in common use in stamp batteries, consisting of shoe, head, stem, and tappet. All these parts are larger in diameter, therefore shorter, than in the ordinary stamp, the centre of gravity hence is lowered. The stamp head is 10 inches in diameter. The stem is of double-faggoted iron 5 to 6½ inches in diameter, and only 10 feet long.

The upper part of the head is made much larger than the other part to give weight, and the resulting shoulder acting in conjunction with the special design of the mortar, forms an efficient baffle to prevent splashing.

The combined weight of the shoe and head is 57½ per cent. of the total weight of a 2,000-lb. stamp.

In 1911 four Nissen stamps of 2,000 lbs. falling weight were run experimentally at the City Deep Mill in competition with a battery of ten stamps of the ordinary heavy Rand type, when the former did considerably better work than the latter.

The duty per stamp per day when using ⅜-inch screen varied from 36·69 to 37·74 tons for Nissen stamps, and for City Deep stamps 22·72 to 24·34 tons.

The power consumption per ton of ore crushed varied from 2·7 H.P. hours to 4 H.P. hours for Nissen stamps and from 4·45 H.P. hours to 5·5 H.P. hours for City Deep stamps.

The wear and tear of shoes and dies is slightly in favour of the Nissen stamp. " These results are considered to be due to the greater facility with which the feed can be adjusted to suit the capacity of each individual stamp in conjunction with the greater screen area resulting from the design of the mortar box." †

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* Rose, *op. cit.*, p. 216.

† Schmitt, *Rand Metallurgical Practice*, vol ii., p. 143.

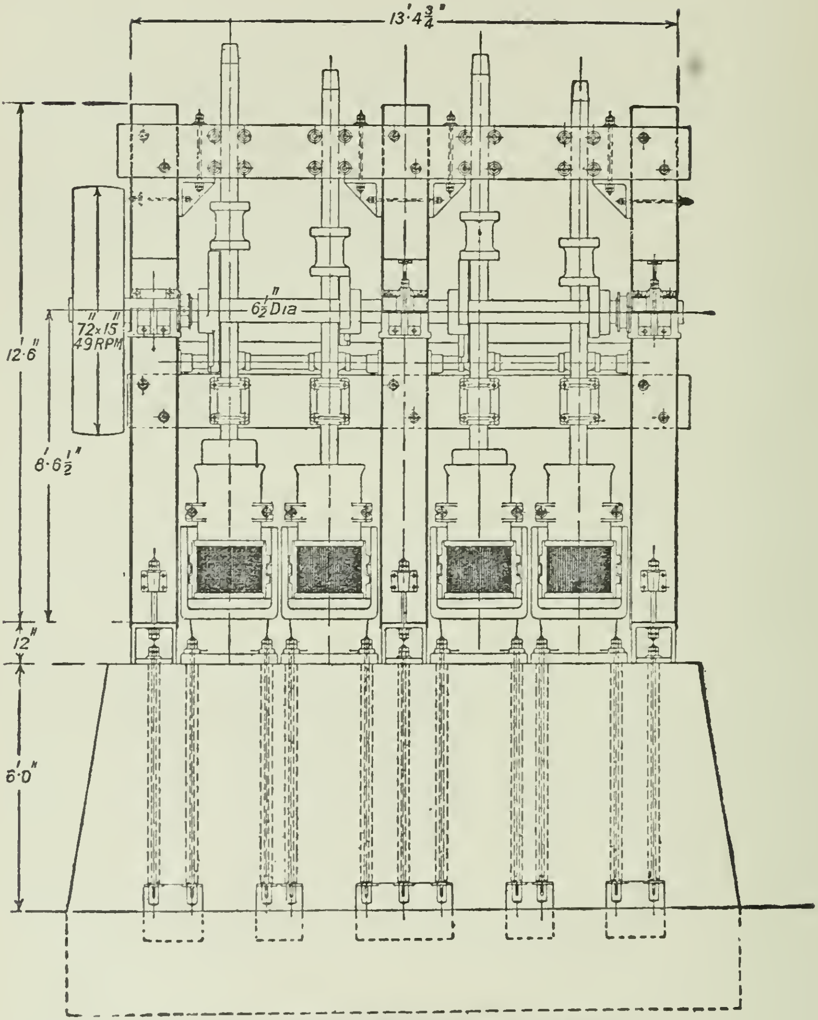
13' 4¾"
6½" Dia
72" x 15"
49 RPM
12' 6"
8' 6½"
12"
6' 0"

Fig. 103.—Nissen Stamp Battery (Elevation).

Nissen stamps have been erected at the City Deep, in some mills in Rhodesia, and at Cobalt, Ontario.

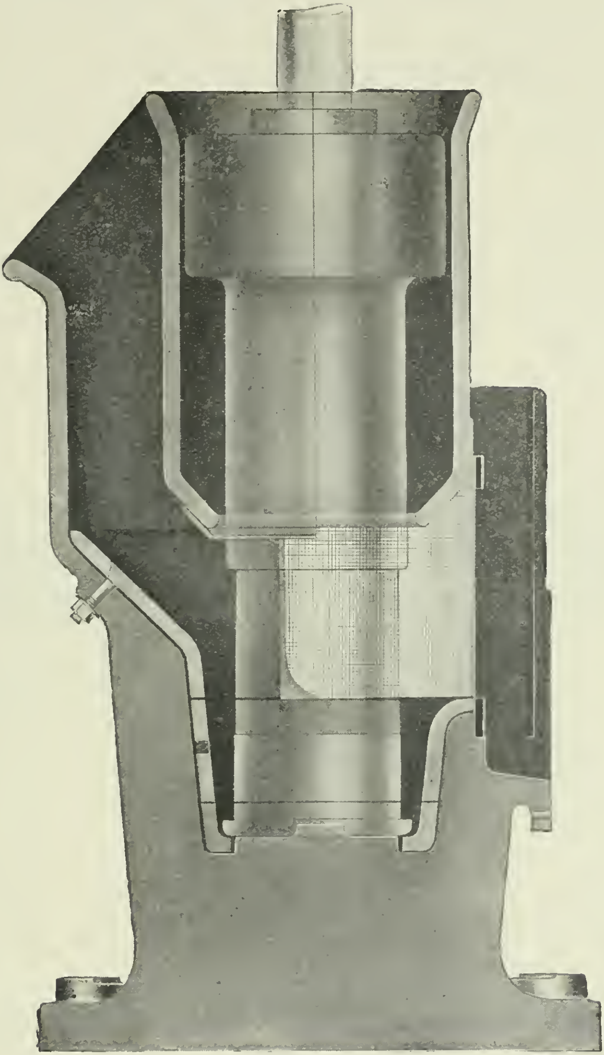

Fig. 103*a*.—Nissen Mortar Box.

The Hardinge Mill.—This mill is a conical tube mill of the shape shown in Fig. 104,[*] and consists of a steel shell lined with silex bricks or hard iron plates or both, and in which the grinding is effected by flint pebbles, steel balls or mine ore, as in an ordinary cylindrical tube mill. When steel balls are used, a steel lining is necessary.

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[*] Rose, *op. cit.*, p. 244.

The pebbles, owing to the shape of the mill, arrange themselves, when it is revolved as shown in Fig. 104, the largest occupy the widest part, and the others gradually diminish in size towards the discharge end. In the ordinary tube mill there is no such arrangement in size, the large and small pebbles are equally distributed throughout the mill, so that the particles of ore after they are crushed fine are still under the action of the largest pebbles, which could otherwise be employed in crushing the coarser fragments of ore.

The action of the Hardinge mill hence differs from that of the tube mill in that the ore fed in passes at once to the horizontal and widest part, where it comes in contact with the largest pebbles falling from the greatest height, and as the particles are broken they pass on to the conical part, where they are subjected to a gradually diminishing breaking force from the smaller pebbles with gradually diminishing fall.

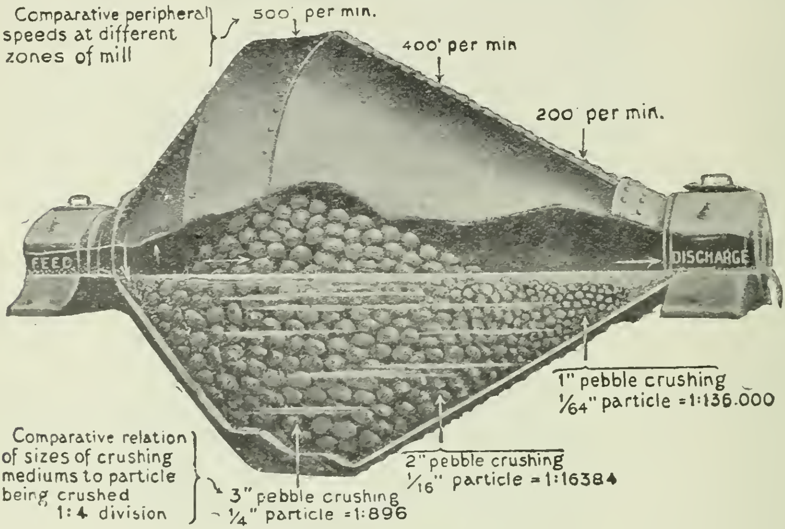
Comparative peripheral speeds at different zones of mill
500' per min.
400' per min
200' per min.
FEED
DISCHARGE
1" pebble crushing 1/64" particle =1:136.000
2" pebble crushing 1/16" particle =1:16384
3" pebble crushing 1/4" particle =1:896
Comparative relation of sizes of crushing mediums to particle being crushed 1:4 division

Fig. 104.—Hardinge Mill.

The shell of the mill is of mild steel plates, in the form of two cones with an intervening cylindrical section. It is supported at each end by a hollow trunnion, through one of which, that at the end of the shorter cone, the ore is fed, and through the other discharged.

The mill is made in several sizes, the cylindrical portion ranging from 4½ to 8 feet in diameter and from 13 inches to 30 inches in length.

The shell is usually lined with silex blocks set in cement, but at the Miami Copper Company's plant, Arizona, the cylindrical portion is lined with cast-iron plates, each plate having a projecting lifter to increase the height of the drop of the pebbles. Pebble linings are also in use.

When a maximum of slime has to be powdered the cylindrical portion is lengthened considerably, even up to 6 feet, the machine then partly assumes the character of a short tube mill. It has, however, been found that the mill is most efficient when producing a fine granular product, with a minimum of slime for concentration.

The output of an 8-foot mill, having a cylindrical portion 30 inches long, will, of course, vary with the nature, hardness, and size of the ore; it will range from 48 to 170 tons per twenty-four hours, the revolutions being 29·8 per minute.*

A motor of about 50 H.P. is required for driving it.

The mill is fed by means of a scoop or spiral feed attached to the inlet trunnion, and the ground ore passes out through the trunnion at the opposite end, the rate of discharge being regulated by the amount of inclination given to the axis of the machine.

The Huntington Mill.—Mills of this type are excellent amalgamators, although probably inferior to stamps.

They cannot be compared with stamps for dealing with hard ores, but are suitable for soft and clayey rock.

The Huntington mill (Fig. 105) consists of a shallow iron pan with a central cone, through which passes an iron shaft carrying a ring B, from which are suspended the stems carrying the crushing rollers E. The shaft is usually driven from below, and by means of it the ring and rollers are revolved. The rollers are so suspended that they swing freely in a radial direction, and are pressed by centrifugal force against the circular die which is fitted to the sides of the pan; they also rotate on their own axes. The rollers, which are of steel, have removable steel shells secured to them by means of wedges. The screens occupy about one-half of the circumference of the pan, and are fixed just above the top of the circular die. The rollers are clear from the bottom of the pan by $\frac{1}{2}$ inch to 2 inches, and in this space the mercury and amalgam accumulate. In starting the mill about 30 to 60 lbs. of mercury are first charged in; then the ore, which has been previously broken to $\frac{3}{4}$-inch cubes, and water are fed through the hopper at the back of the pan. Small quantities of mercury are added from time to time. The ore is thrown against the die at the sides by the revolution of the suspended rollers, and is crushed between it and the rollers by centrifugal force. The crushed ore is delivered through the screens into the outside gutter, whence it passes to the amalgamated table in front. Screens in which the wires are diagonal have the longest life.

The capacity of a 5-foot mill with hard ores will be about 10 tons, and with softer ores 20 tons, through a 30-mesh screen, in 24 hours.

The number of revolutions ranges from 50 to 85 per minute.

The advantages of the Huntington mill, as compared with stamps, are:—

1. Lower first cost.
2. Less time and cost in erection.
3. Does better work on soft ores and in regrinding coarse tailings.
4. Less power per ton of ore crushed.
5. Less flouring of amalgam and mercury.

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* Rose, *op. cit.*, p. 245.

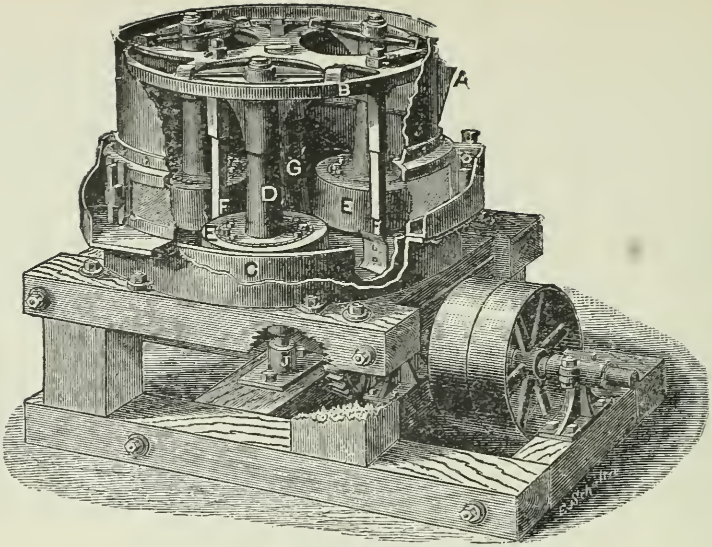
A
B
G
D
F
E
E
F
C
J

Fig. 105.—The Huntington Mill.*

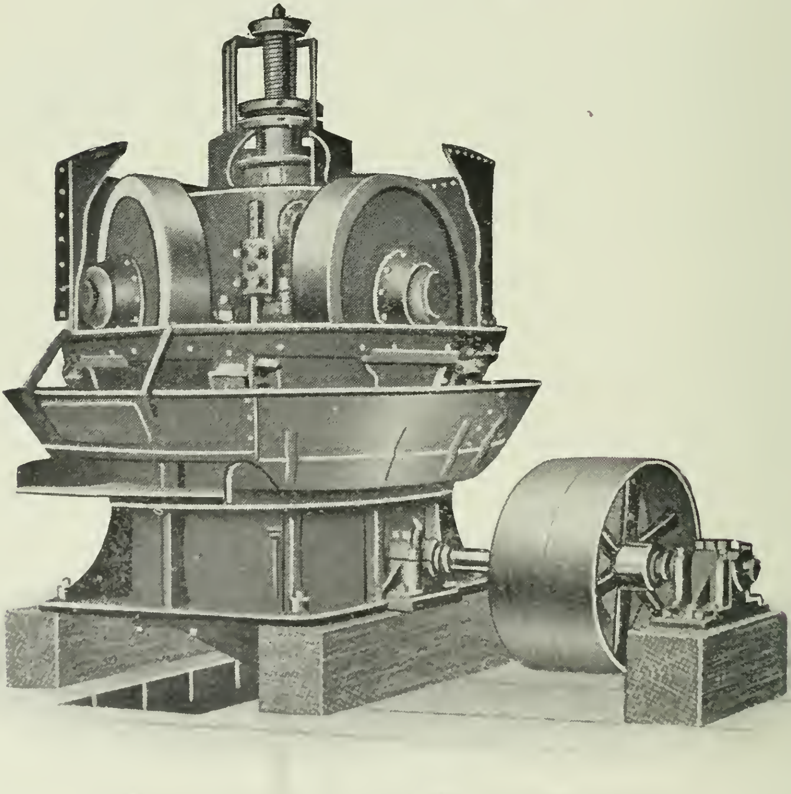

Fig. 106.—The Evans-Waddell Chilian Mill (Fraser and Chalmers).

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* Rose, *Gold*, p. 219.

Disadvantages :—

1. Less reliable.
2. Not suitable for hard quartz.
3. Not suitable for very large outputs.
4. Uneven wearing of the roller rings, resulting in deficient grinding.

The Chilian Mill.—Improved forms of this old mill, one of which is shown in Fig. 106, have been introduced into the United States for the fine grinding of ores, to prepare them for treatment by the cyanide process.

As regards slow-speed Chilian mills, H. A. Megraw says :*—" In cases where leaching is possible, I can imagine nothing more simple or economical both to instal and to operate than the Chilian-mill plant, which takes its feed directly from the breaker and delivers directly to the treatment system after classification."

Amalgamation in Pans.—Pan amalgamation was once practised to a considerable extent for the treatment of ores, which did not readily yield their gold to the amalgamated plates of the stamp battery, or ores containing much silver, and of blanket sands and concentrate. The pans and methods of treatment were similar to those employed for silver ores (p. 382). Grinding and amalgamation in pans has, however, been practically given up, except for the treatment of the coarser sands in cyanide plants, especially in W. Australia.

CHLORINATION.

The process of chlorination depends on the fact that chlorine has a strong affinity for gold, and readily combines with it to form soluble gold chloride. The solution can be run off from the residue, settled and filtered, and the gold contained in it precipitated by suitable reagents.

Chlorination was given up in 1912 at the largest plant in Colorado, where the process had been long in use, and in the same year the last mill treating Cripple Creek ores by chlorination was converted into a cyanide mill.

In other districts, too, it has been replaced by the cyanide process, and is now practically obsolete. In a few mills it is retained for the treatment of pyritic concentrate from stamp milling, but for this purpose cyaniding or smelting will generally be found to be more efficient and economical. When much silver was present barrels were employed, as the agitation removes the coating of AgCl which forms on the particles of gold and prevents the action of the chlorine, or the silver was first separated by the hyposulphite process.

Other ores for which chlorination was used were those consisting mainly of limonite or hydrated oxide of iron, which resist amalgamation. Also, rich ores in which the gold was in a very fine state of division. One of the chief disadvantages of chlorination, as compared with the cyanide process, is the cost of the preliminary roasting which is always necessary, while recent work done in S. Africa and elsewhere has shown that ores generally, and even concentrate, when slimed, will yield a high percentage of their gold when cyanided without roasting.

Chlorination is carried out by three methods :—

1. The *Vat or Plattner process*, in which the moistened ore placed in vats is acted on by chlorine gas.

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* *Eng. and Min. Journ.*, November, 1913, p. 921.

2. The *Barrel or Thies process*, in which the ore together with water is placed in a revolving barrel, and is acted on by chlorine generated in the barrel itself.
3. The *Vat-solution process*, in which the ore placed in vats is acted on by moderately dilute solutions of chlorine.

The operations required are :—

1. Crushing in the case of ores.
2. Roasting with or without common salt.
3. Chlorination and lixiviation.
4. Precipitation of the gold in the state of metal, or as sulphide.
5. Conversion of the precipitated gold into bullion.

Crushing.—The crushed ore must be in a sufficiently fine state of division to expose the whole of the gold to the action of the chlorine, yet it must be sufficiently coarse and free from slime to permit rapid lixiviation.

Dry crushing is advantageous, as the ore has always to be roasted.

The ore is generally crushed to pass screens ranging from 15 to 30 mesh.

A common practice was to crush in a rock breaker to $\frac{1}{2}$-inch cubes, and pass the material first through coarse rolls, set about $\frac{3}{16}$ inch apart, and then through fine rolls set to the required mesh.

Roasting.—The object of roasting is to expel sulphur, arsenic, antimony, and other volatile substances present in the ore, to oxidize the base metals, and as far as possible leave nothing which can combine with chlorine except metallic gold. Ores containing calc spar, magnesium carbonate, galena, or copper pyrites must be roasted with common salt ($NaCl$) to convert the metals into chlorides, otherwise chlorine will be wasted. If silver is present, and has to be extracted, roasting with salt is necessary to convert it into chloride, so that it may be leached out with sodium hyposulphite.

When the ore only requires an oxidizing roast, without the addition of salt, the loss of gold is small, providing that due care is taken to avoid dusting and too high a temperature.

The greater the amount of base metals in the ore, the greater will be the loss. A high temperature will cause a greater loss of gold than prolonged roasting at a low temperature.

When, however, roasting with salt is necessary, the loss of gold may be very great.

The quantity of salt used must be as little as possible, and it should not be added until near the end of the operation, when nearly all the sulphur has been expelled, and the temperature then should be reduced. But, in spite of all precautions, there will always be some loss, especially when copper is present, as copper chloride in volatilizing carries off gold.

The reactions which occur in oxidizing roasting are described under "Copper" (p. 71), and those in chloridizing roasting under "Silver" (p. 390)

The furnaces required are any that are suitable for chloridizing roasting.

The Vat Process.—The vat process is specially suitable for small mills. As ordinarily practised, it consists of the following operations :—

1. The ore, after roasting, is slightly moistened with water and charged into a wooden vat with a false bottom of perforated boards supporting a filter bed of gravel, or crushed quartz. The vat is then closed by a cover, which can be luted to its upper edges. The chlorine is generated in a separate vessel, and is passed into the vat through an aperture below the false bottom.

2. When the ore has been thoroughly impregnated with chlorine, and has stood for 24 to 48 hours, water is run on, and the gold chloride leached out.

3. The solution is run into a settler, and through a filter into a wooden vat, in which the gold is precipitated by ferrous sulphate.

4. When a sufficient quantity of the precipitate has accumulated it is collected, dried, melted with fluxes, and cast into ingots.

The vats (Fig. 107) are built of 2-inch pine staves, and are coated with pitch and tar, or with asphalt. They range in size from 8 to 9 feet in diameter and 3 feet to 3 feet 6 inches in depth, holding respectively 3 and 4 tons of ore.

The false bottom consists of 1-inch boards perforated with ½-inch holes, resting on 1-inch strips. Upon this the filter bed, 6 to 12 inches in thickness, is made of quartz pebbles or crushed quartz, beginning at the bottom with coarse material, and gradually increasing the fineness until the top consists of about 2 inches of fine sand. Canvas cloth or cocoa matting, in a frame, is fixed over the sand, and over this is laid a lattice work of wood, to prevent the filter bed from being injured in shovelling out the spent ore.

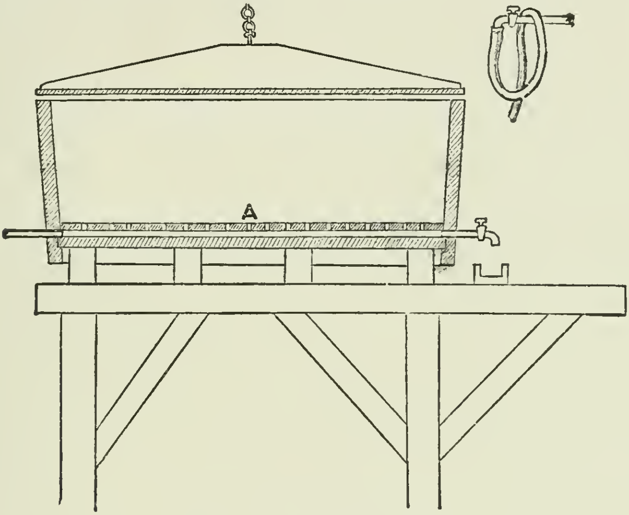

Fig. 107.— Chlorination Vat.*

There are two apertures in the vat below the filter bed, one in the side for the admission of the chlorine, and the other in the side, or bottom, through which the solution is run off.

In charging the vat sufficient dry ore to absorb the water in the filter must first be thrown in, otherwise the lower layers of ore will be too wet, and the passage of the chlorine will be hindered. The properly dampened ore is then put in through a coarse sieve (No. 4 or 6 mesh), to ensure the requisite porosity of the charge.

The vat is filled to within 6 inches of the top. The cover is then lowered and luted to the top of the vat with clay, the joint being prevented from cracking by wet rags. The chlorine is then passed in until it is found to be in excess on testing with ammonia at a small aperture in the cover, the time required being from five to eight hours.

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* Rose, *op. cit.*, p.303.

The chlorine generator is a leaden vessel, which is set on a sand bath, or on a water bath, which is better, as the heat required is not more than 90° C. It is fitted with a stirrer, the shaft of which passes through the middle of the heavy lead cover. Both the cover and the shaft have water seals, to prevent the escape of the gas. The charge for 3 tons of ore is given by Rose as 20 to 24 lbs. of rock salt, 15 to 20 lbs. of manganese dioxide (70 per cent.), and 35 lbs. sulphuric acid of 66° B. (sp. gr., 1·842) diluted with half its *weight* of water. The gas is passed through a wash bottle before being led to the vat. The reaction is as follows :—

$$2NaCl + MnO_2 + 2H_2SO_4 = Cl_2 + Na_2SO_4 + MnSO_4 + 2H_2O.$$

After the introduction of the gas has been stopped, the charge is left undisturbed for 24 to 48 hours, and at some works fresh gas is introduced a few hours before leaching.

The cover is then removed and water is run in carefully, usually on a layer of sacking, spread over the ore to distribute it evenly, until it covers the ore to a depth of about 3 inches. After standing for about half-an-hour or an hour the solution is allowed to run off, water being added to keep the top of the ore covered. The leaching is continued until the solution gives no indication of gold on being tested with iron sulphate.

The solution is run either into a settling vat, and then through a filter bag of canvas, or through the latter only, into the precipitating vat. The precipitating vat is about 5 to 7 feet in diameter, 3 feet in depth, and is best made wider at the bottom than at the top, so that the precipitate may not lodge on the sides.

If the solution contains lead or lime sulphuric acid is added to precipitate them as sulphates, and after settlement the clear liquid is run into another vat, in which the gold is precipitated.

The iron sulphate is usually introduced into the vat as soon as the gold solution begins to run in.

The solution is vigorously stirred with wooden paddles, to facilitate the settlement of the gold. The reaction is as follows :—

$$2AuCl_3 + 6FeSO_4 = Au_2 + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$

Additions of ferrous sulphate are made until no colouration of the solution is produced. The precipitated gold is allowed to settle for 24 or 48 hours, and the supernatant liquid is then drawn off by means of an india-rubber tube, the inlet end of which is kept near the surface by a wooden float (see p. 418).

It should be passed through a charcoal box filter, to catch any gold which may not have settled.

The precipitate is not removed until sufficient has accumulated after several charges of solution have been precipitated.

When a clean-up is made, the precipitate is drawn off and passed through a filter press, or if in small quantity may be filtered through paper.

When much oxide or basic salts of iron are present it is treated with hydrochloric acid.

After drying it is fused with borax, sodium chloride, potassium nitrate, etc., and cast into ingots.

The extraction, when carefully carried out, and interfering substances are not present to any considerable extent, ranges from 90 to 95 per cent.

If much silver is present, it can be separated and recovered by leaching the residues with sodium hyposulphite. In some cases, the silver is similarly extracted immediately after the roasting, and before the ore is treated with chlorine, but then the ore or material must be partially dried before charging into the chlorination vats.

Instead of generating the chlorine at the mill, liquid chlorine has been used, as at the Utica Mine (Cal.).

The Barrel Process.—In 1898 this process had reached its highest development in the Cripple Creek district, but since that date chlorination has been given up there, and cyaniding adopted. When chlorination is practised, the barrel process is especially suitable if a large output has to be obtained.

Chlorine is generated in the barrels by using bleaching powder and sulphuric acid.

The barrels are fitted with an internal filter, so that the ore is chlorinated, leached, and washed in the barrels themselves. They vary in size from 12 feet by 6 feet, with a capacity of 8 to 9 tons of ore, to 16 feet by 5½ feet, holding 12 tons. Barrels holding 18 tons were also in use at Cripple Creek.

The shell is of ⅝-inch mild steel, and the ends of cast iron heavily ribbed. They are designed to withstand a pressure of 100 lbs. per square inch. The lining is of 24-lb. lead—*i.e.*, ½-inch in thickness.

The filter consists of a finely perforated sheet of 4- to 6-lb. lead, laid on lead plates ½ to ¾ inch thick perforated with ⅜-inch holes, and held together by two gratings of hard wood.

The whole is held in place by cross bars keyed under side bars bolted to the shell of the barrel. Asbestos cloth has been used in place of the lead, but it has a shorter life. There are two charging holes in the top of the barrel above the filter, and a discharge opening below for the discharge of the solution and washings.

The barrel is charged by first running in the amount of water required to make the ore free flowing. The sulphuric acid is then cautiously poured in, so that it sinks below the water without mixing with it.

The ore is then charged from the hopper above the barrel through two shoots, and the bleaching powder added on the top of the ore. The amount of bleaching powder and sulphuric acid depends on the composition of the roasted ore. At the Valley Custom Mills, Cripple Creek, 100 to 200 lbs. of bleaching powder (30 to 33 per cent. Cl) and 300 to 400 lbs. of sulphuric acid (60° B.) were used in 1905.

The equation representing the action of the acid on the bleaching powder is usually given as follows :—

$$CaOCl_2 + H_2SO_4 = Cl_2 + CaSO_4 + H_2O.$$

But much less chlorine is given off, as bleaching powder usually contains only from 25 to 35 per cent. of chlorine.

The barrel is now revolved at the rate of from 4 or 5 to 12 revolutions per minute for from 3 to 4 or sometimes 6 hours. The chlorine must be present in excess, and this is ascertained from time to time by holding a rag wetted with ammonia solution opposite a small valve, which is opened momentarily. When the chlorination is complete, the barrel is stopped, with the filter downwards, and allowed to rest for a short time to allow the pulp to settle. A hose is then attached to the discharge pipe, the cock opened, and the solution allowed to run out. Water is then pumped in under pressure to wash the solution of gold chloride out of the pulp. The washing is then stopped temporarily, and the barrel revolved. More water is then pumped in, the barrel again revolved, and this is repeated until the washings no longer contain gold. The gold solution and washings are run by means of the hose pipe to settling tanks lined with lead, and when settled the clear liquid is transferred to the precipitating vat.

The tailings are discharged, either into a sluice, down which they are washed with water, or into a car by which they are taken to the dump, or, in some cases, as at Cripple Creek, they were concentrated on Wilfley tables and the concentrate was sent to a cyanide plant for the further extraction of gold.

Where ores are treated in large quantities the precipitation of the gold is usually effected by sulphuretted hydrogen, as the precipitate produced by ferrous sulphate requires a long time for subsidence, and is difficult to collect in a filter press.

As sulphuretted hydrogen is decomposed by chlorine, sulphur dioxide was first passed in when the following reaction took place :—

$$Cl_2 + SO_2 + 2H_2O = H_2SO_4 + 2HCl,$$

and not until all the chlorine had been thus converted into hydrochloric acid was sulphuretted hydrogen introduced into the solutions. But recently the use of SO_2 has been abandoned, and sulphuretted hydrogen is passed in at once. It is usually forced in mixed with air, which assists in stirring the solution, when the following reaction occurs :—

$$2AuCl_3 + 3H_2S = Au_2S_3 + 6HCl.$$

By careful management the gold can all be perfectly precipitated and the copper be left in solution. When the precipitate has settled the supernatant liquid is run through a filter press. The precipitate is allowed to accumulate until several charges have been treated. It is then transferred to a filter press. (If much base metal is present ferrous sulphate is sometimes used.) The filtrate from the press is run through a sand-box filter. The cakes of gold sulphide from the press are placed on an iron tray, and taken to a furnace containing a cast-iron muffle, in which the sulphur is burnt off at a low red heat.

The roasted precipitate is mixed in the tray with the necessary fluxes, usually borax, sodium carbonate, and potassium nitrate, the mixture charged into a crucible, melted, and cast into ingots.

The gold may be about 900 to 950 fine.

The Vat Solution Process.—This process was carried on on the largest scale at the Mt. Morgan Mine (Queensland), but has been given up.

The ore from the upper levels was of low grade, containing only 4 to 5 dwts. of gold, and sulphur was only present to the extent of 2 per cent. As the workings became deeper the gossan gave place to a siliceous gold ore charged with copper pyrites, the chlorination process has hence been relinquished, and the ore is to be treated by smelting.*

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* *Min. Mag.*, vol. vii., pp. 175 and 231 (1912).

As the chlorination plant was the best arranged for carrying out the "vat solution process," a brief description of it will be given.

The ore was ground in ball mills to pass through a 20-mesh screen. It was roasted in revolving cylindrical furnaces with continuous discharge, merely to dehydrate the kaolin which was present, and thus facilitate the leaching. The leaching vats were of brick, 60 feet long, 12½ feet wide, and 6 feet deep, their capacity being about 200 tons. Each was fitted with a filter bed of sand and gravel, resting on perforated planks supported by bearers. The roasted ore was distributed to the vats by push conveyors, or cars, and levelled.

The solution of chlorine was then run on, and when the vat was full the discharge valve was opened and the liquid drawn out slowly by a vacuum pump and delivered to storage vats. The chlorine solution was added until the gold was dissolved. A water-wash was then given until on testing with ferrous sulphate the washings gave no indications of gold.

The gold solutions from the storage vats were run to charcoal filters. The filters, 10 feet by 12 feet by 5 feet, were built of brick and lined with cement and tar. The filter consisted of a layer of charcoal, not less than 2 feet thick, supported on the usual filter bottoms, and covered with heavy perforated sheets of lead. The solutions were passed through three filtering vats in succession, and when sufficient gold had accumulated in the filters the charcoal was dried and burnt and the ashes were fused with soda ash and borax to obtain the bullion in the form of ingots.

The chlorine was generated in stills, made of slabs of sandstone, from manganese ore, salt, and sulphuric acid. The gas was led in earthenware pipes to scrubbing towers, 20 feet high, 2 feet 3 inches in diameter, filled with glass bottles and old assay crucibles, over which water was kept trickling. The solution of chlorine thus obtained contained not less than 80 grains of chlorine per gallon.

The extraction is said to have been 95 per cent. of the gold contained in the ore.

The Cyanide Process.—The process consists in treating ores or tailing carrying gold and silver, with solutions of potassium cyanide containing generally much less than 0·5 per cent. of the salt. These weak solutions readily dissolve gold and silver and, with the exceptions mentioned below, in preference to base minerals. Sodium cyanide (equivalent to 129 to 130 per cent. of KCy) is the form in which cyanide is used in most mills; it has, however, been objected to for some ores.

When the ores or tailings, however, are acid, or iron or copper sulphates are present, from the oxidation of the pyrites which they contain, they are submitted first to a water wash and subsequently to an alkaline wash with soda or lime, otherwise there will be a great waste of cyanide.

The gold dissolved in the KCy solutions is precipitated from them by zinc shavings, zinc dust, or electrolytically. The process, as compared with chlorination, has several important advantages, viz.:—

1. Roasting is not necessary, even when pyrites are present. This is important in low-grade ores, which cannot bear the cost of the operation.

2. The cost of chemicals is lower, hence it is specially suitable for low-grade ores.

3. Silver is extracted as well as gold.

4. In chlorination the base metals are preferably attacked by the chlorine

rather than the gold, while in cyaniding the reverse is the case, especially when dilute solutions of potassium cyanide are used.

It is difficult to say with absolute certainty whether or not a given ore can be profitably treated by the cyanide process. Actual tests are necessary in each case.

The following ores, however, are, as a rule, suitable for treatment :—

1. Ores in which the gold occurs in a very finely divided state, and in which base minerals are absent, or present only in very small quantities. When both coarse and fine gold are present the coarse gold may be extracted in the stamp mill by amalgamation before cyaniding.

2. Tailing from stamp battery amalgamation.

3. Ores containing iron pyrites in which the gold is not finely disseminated, but occurs coating the crystals, or between the crystalline planes.

4. Ores and concentrate, in which the gold exists finely disseminated in pyrites, can be treated, but either extremely fine grinding or special treatment is necessary.

5. Argentiferous gold ores free from interfering substances, but extra strong solutions and prolonged leaching are required.

6. Ores in which the gold resists amalgamation owing to the existence of a thin film of some substance which covers its surface, the so-called "rusty gold."

7. Silver ores.

The ores and tailings which are difficult to treat, cause excessive consumption of cyanide, and require special modifications of the ordinary process, may be classified as follows :—

1. Old tailings and weathered ores in which the pyrites they contain have been more or less oxidized. In these there may be present sulphuric acid and copper and iron sulphates, all of which destroy cyanide.

It is hence necessary to remove the free sulphuric acid and soluble sulphates by leaching with water, and then to run on a lime or soda solution, lime being generally preferred. A preliminary water wash is advisable, as if the alkaline wash is first run on, the sulphates are decomposed, hydrates being formed which are soluble in KCy, and are dissolved in preference to the precious metals.

A common practice, however, is to add lime to the tailing before charging into the vats, or to feed it into the stamp battery with the ore.

Pure cubical iron pyrites is said by Skey to have almost no action, if any, on potassium cyanide solutions. Zinc blende, too, acts but slightly.

2. Ores containing copper carbonates and sulphides, copper pyrites, marcasite, and calamine. These, when present in an ore, give rise to an excessive consumption of cyanide.

The copper of carbonates and the zinc of calamine combine with KCy to form double cyanides, but as sulphides they dissolve but slowly until oxidized. Marcasite is especially objectionable, as it is so readily decomposed producing ferrous sulphate and sulphuric acid. Clean galena unoxidized is only slightly acted on by cyanide.

3. Ores containing stibnite. According to Skey, the sulphur tends to combine with the potassium of the cyanide, also to form sulpho-cyanogen, and much cyanide is destroyed, yet in Upper Sarawak an ore with 5 dwts.

gold per ton, on the average, and 11 per cent. of stibnite, yields 75 per cent of its gold to weak solutions of cyanide.*

4. Ores containing tellurides are not amenable to cyanide treatment unless they are first roasted or bromo-cyanogen is used together with potassium cyanide.

There are five distinct chief classes of operations in the process :—

(*a*) Preparation of the ore by breaking, crushing, and grinding with or without amalgamation and tube milling.

(*b*) Leaching sands with weak solutions of sodium or potassium cyanide.

(*c*) Treatment of slimes.

(*d*) Precipitation of the gold by zinc or zinc dust.

(*e*) Treatment of the precipitated gold to convert it into bullion.

Preparation of the Ore.—The following methods for the preparation of the ore are those in general use :—

1. Crushing in stamp batteries having 20 to 25 mesh screens.

Extracting the coarse gold by amalgamation either inside the mortars and subsequent passage of the pulp over amalgamated plates, or by the latter only. In some plants, mostly small, Huntington mills are used instead of stamps.

2. Crushing as above, but through coarse screens, ranging from 10 mesh to 3 mesh, followed by grinding in tube mills (S. Africa) or grinding pans (Australia) and amalgamation of the pulp from these. Ores for the latter are generally passed through 15 to 20 mesh screens. For tube mills $\frac{1}{4}$-inch particles are said to be best.

3. Crushing and grinding as in 2, and converting the whole of the ore into slime. S. Africa, Mexico, etc.

4. Crushing the ore in cyanide solution, part or the whole of the ore being converted into slimes by grinding. S. Africa, Homestake Mine, S. Dacotah, etc.

5. Dry crushing by stamps, rolls, or ball mills. The last two especially have been sometimes adopted where the ores are treated direct by cyanide without preliminary amalgamation.

" At the present day on the Rand † the use of the tube mill is acknowledged to be indispensable for reducing the coarser particles of the ore leaving the stamp battery to the fineness required for effective treatment in the cyanide plant, which may be assumed to be as follows :—

" Not more than 1 per cent. to remain on a 60-mesh screen (aperture ·01 inch), and fully 90 to 93 per cent. to pass a 90-mesh screen (aperture ·006 inch).

" The best performance of stamps and tube mills in combination has so far been obtained at the East Rand Prop. Mines, where, by eliminating the $-\frac{3}{8}$ product from the ore feed to the stamp mill and feeding the same direct to the tube-mill plant, 10 stamps of 1,600 lbs. falling weight and one tube mill of standard size (22 feet long by 5 feet 6 inches diameter) crush 257·5 tons per day, the final pulp containing 94 per cent. of — 90. Twelve crushing sets of this type are already in regular use, handling over 3,000 tons per day. The fine ore is screened before reaching the mortar box by a small trommel, having a shell of screening with ·32-inch aperture, the same as used in the mortar box."

The latest practice in the amalgamation of gold from banket ore as adopted in the latest plants is illustrated in Figs. 119 and 120. Amalgamated plates have been eliminated from the battery, except in the older plants, and are now only used after the tube mills.

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* *Trans. Inst. Min. and Met.*, vol xv., p. 63, *et seq.*

† *Rand Metallurgical Practice*, vol. ii., pp. 63 and 65.

At Cripple Creek, practice is divided between rolls and ball mills. In Australia, and many American mills, ball mills are in extensive use, generally preliminary to roasting. With dry crushed ores the cyanide solution is not diluted, and percolation is easy.

At the present time the tendency is towards abolishing amalgamation, at least at the battery, also concentration, and treating the ores simply by the cyanide process after grinding to an impalpable paste subsequently treated by agitation and filter pressing. On the Rand, and at some mills elsewhere, however, amalgamation on plates is practised after tube milling.

There are many variations in the mode of conducting the cyanide process, and in many cases they are not based on the character of the ore, the same ore receiving different methods of treatment at different mines.

The following methods are those which are chiefly employed :—

I. *Simple Cyaniding.*—When the ores consist of pure quartz or quartzose material, contain no substances which destroy cyanide, and in which the gold is in a fine state of division, and also which give but little slime in crushing, thus admitting of easy percolation, this method is practised, and is also followed for sand generally. The screens used in the stamp battery range from 20 to 40 mesh. These ores, however, are not common, so that almost everywhere the cyanide process is much more complicated. The gold is precipitated from the solutions in zinc boxes.

II. Cyaniding of sand as in I., with previous amalgamation in the stamps and on apron plates. Suitable for the above ores when they contain both finely divided and coarse gold. Amalgamation is necessary, as the particles of coarse gold would require too long a time to dissolve in cyanide solutions.

III. Cyaniding of sand and slime, the following operations being required :—

(*a*) Crushing the ore by heavy stamps, using a coarse mesh screen.

(*b*) Fine grinding of the pulp in tube mills or grinding pans with or without amalgamation.

(*c*) Separation of sand and slime in classifiers, with sometimes separation of pyritic concentrate by tables or vanners.

(*d*) Leaching the sand as in I.

(*e*) Agitation of the slime with cyanide solutions and separation of the gold solutions by decantation, now being given up (p. 305), vacuum filters (p. 316), or filter pressing (p. 323). Suitable for most ores, and in extensive use.

(*f*) Precipitation of the gold in zinc boxes or with zinc dust.

IV. All sliming method.

(*a*) Crushing as in III.

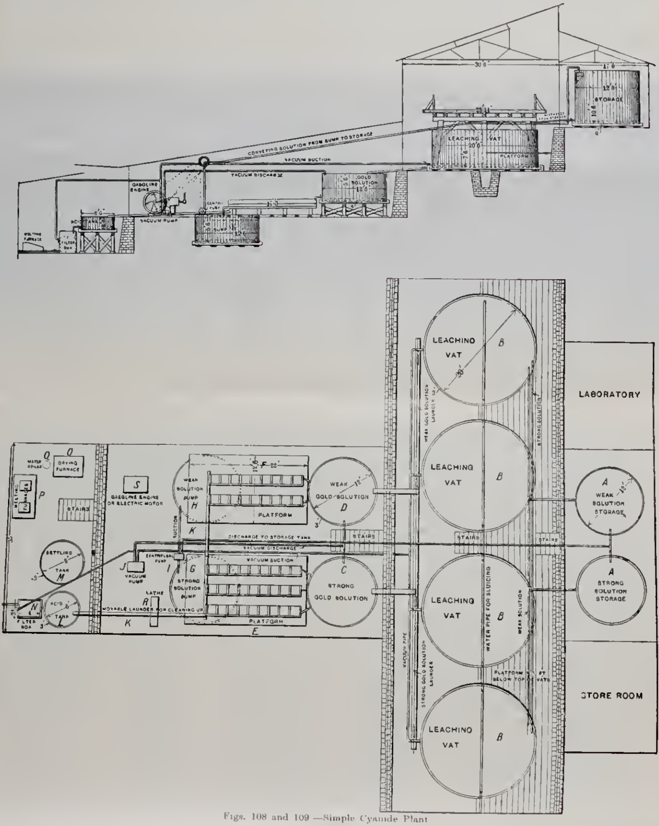
(*b*) All-sliming of the pulp generally in tube mills, at some mines in grinding pans, with or without separation of pyritic concentrate.

(*c*) Amalgamation of the product from the tube mills on apron plates, or amalgamation by introducing mercury into the pans.

(*d*) Treatment of the slimes and gold solutions, as in III.

V. Cyaniding ores containing tellurides or sulpho-tellurides by either of the following methods :—

(*a*) Dry crushing, all-roasting, all-sliming in grinding pans with amalgamation, agitation, and filter pressing. (The Marriner process.)


STORAGE
LEACHING VAT
PLATFORM
CONVEYING SOLUTION FROM SUMP TO STORAGE
VACUUM SUCTION
VACUUM DISCHARGE
GOLD SOLUTION
GASOLINE ENGINE
VACUUM PUMP
SUMP
ACID TANK
FILTER BOX
MELTING FURNACE
LABORATORY
STORE ROOM
WEAK SOLUTION STORAGE
STRONG SOLUTION STORAGE
A
B
C
D
E
F
G
H
I
J
K
L
M
N
O
P
Q
R
S
STRONG SOLUTION
WEAK SOLUTION
WATER PIPE FOR SLUICING
PLATFORM 3 FT BELOW TOP OF VATS
WEAK GOLD SOLUTION LAUNDER
STRONG GOLD SOLUTION LAUNDER
VACUUM PIPE
STAIRS
WEAK GOLD SOLUTION
STRONG GOLD SOLUTION
DISCHARGE TO STORAGE TANK
VACUUM DISCHARGE
VACUUM SUCTION
WEAK SOLUTION PUMP
STRONG SOLUTION PUMP
CENTRIFUGAL PUMP
SUCTION
GASOLINE ENGINE OR ELECTRIC MOTOR
LATHE
MOVABLE LAUNDER FOR CLEANING UP
DRYING FURNACE
WATER SCALES
MELTING FURNACE
SETTLING TANK
ACID TANK
FILTER BOX

Figs. 108 and 109 —Simple Cyanide Plant

(*b*) Wet crushing in cyanide solution, classifying, concentrating, all-sliming in grinding pans or tube mills, or in both, agitation with cyanide and cyanogen bromide, and filter pressing. The concentrate is roasted, slimed, and amalgamated in grinding pans, agitated with cyanide, and filter-pressed. (The Diehl process.)

Simple Cyaniding.—The simplest possible form of a cyanide plant is shown in Figs. 108 and 109.* It is only suitable for the treatment of sand, or tailing which does not contain slime in sufficient quantity to interfere with percolation.

There are two storage tanks A, A for the cyanide solutions, one for the weak and the other for the strong.

Each is connected by means of launders or pipes with the leaching vats B, B, B, B, so that either strong or weak solution may be run into any of them as desired. They are also respectively connected by pipes with the sumps G, H for the strong and weak solutions, in order that these solutions may be returned to them by the centrifugal pump I. A small tank is sometimes provided for dissolving the cyanide necessary to bring the solutions to the proper strength. The leaching vats B, B, B, B are about 20 feet 6 inches in diameter by 7 feet deep, and hold about 75 tons of sand. Each has the usual filter frame (see p. 297), with a discharge pipe below it. This pipe is fitted with two cocks, so arranged that it can deliver the gold solution into either of the launders or pipes in front, one of which leads to the strong gold solution vat C, and the other to the weak solution vat D, for the settlement of any fine ore which may have passed through the filters.

There is also an opening in the bottom of each vat for the discharge of the spent residue.

From the vats C, D the clear solutions are run off to the zinc boxes E and F, in which the gold is precipitated, E being for the strong and F for the weak solutions.

The solutions from the zinc boxes pass respectively to the strong and weak solution sumps G and H, from which they are pumped back to the storage tanks A, A.

At the clean-up the zinc box precipitate is conveyed by the launders K, K to the acid vat L. The adjoining vat M is used as a settler for the liquors and washings from the treatment of the precipitate in L. The washed precipitate is collected in the filter press N, dried or roasted in the furnace O, and melted with fluxes in the furnaces P. (For details of the treatment of the precipitate, see p. 334).

Q is a boiler for the wash-water, S the engine or motor for driving the pumps, etc., and R a lathe for cutting the zinc shavings.

Simple Treatment.—This is only possible for the product of the stamp mill when it contains slime in such a small amount that it can be leached.

The ore having been prepared by crushing by stamps or otherwise, as described on p. 279, the leaching is usually carried out as follows, but the procedure is more or less modified at different works :—

The leaching vats are filled with the crushed ore from side-tipping cars running on an overhead railway, the supports for which must be independent of the vats to avoid any jarring, as this leads to packing and irregular leaching. The ore must be carefully levelled with hoes, the labourers working from outside the vat, and the amount charged in should be such that, after the solutions have been run in, the level of the charge will be from 10 to 12 inches below the rim. If the charge contains soluble salts, or acid from the decomposition of pyrites, a water-wash is given, the water being added below the filter. This is then followed by a wash also from below of soda or lime, lime being preferred in S. Africa.

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* F. L. Bosqui, "Practical Notes on the Cyanide Process," p. 40.

A weak solution of cyanide from the sump is now sometimes applied to displace the water from the previous washings. The strong solution, about 0·15 to 0·25 per cent. KCy, is now run on to the top of the charge, until it stands about 3 inches above it.

In some cases the strong solution is allowed to remain on the charge for several hours before percolation, otherwise the discharge cocks are set, so that drainage takes place regularly during 24 hours. This operation is sometimes repeated, and it has occasionally been found advisable with some ores to allow the percolation to be rapid, and to pump back the solution to the top of the charge (circulation method).

The ore is now allowed to drain completely to permit access of air, as the presence of a certain amount of oxygen is essential to the solution of gold in KCy. The weak solution 0·05 to 0·1 per cent. KCy is then run on, the quantity ranging from twice to four times the amount of the strong solution. Finally the charge is treated with successive washes of water, in the ratio of about 1 water to 6 to 10 of ore, which are allowed to percolate rapidly, aided by a vacuum pump.

The spent residue is then discharged through the discharge opening into trucks below. The various solutions after settlement in the gold solution vats pass to the zinc boxes, solutions containing over 0·15 per cent. KCy generally going to zinc box E, and those below to F. The clean-up of the zinc boxes and the treatment of the precipitate are described on pp. 331 to 336.

The simple cyanide method of treatment just described is, however, altogether inadequate for modern requirements, hence during recent years more complicated arrangements both in plant and practice have been introduced in all the chief mining districts.

The most important changes are the following:—

1. Increase in the weight of stamps and in screen aperture.
2. The adoption of classification in cones and other apparatus to the displacement of the old spitzkasten.
3. The extension of tube milling.
4. The development of agitating and filtering apparatus.
5. The introduction of zinc dust instead of zinc shavings for the precipitation of gold.

The increase in the weight of stamps, especially in S. Africa, has already been pointed out (p. 259); also, that since the introduction of tube mills in cyanide plants the function of the stamp battery is merely to crush the ore to about $\frac{1}{4}$ inch to prepare it for these machines.

The result of this coarse crushing by stamps, combined with a final reduction in tube mills, has been to increase very largely the output as well as to effect a greater extraction of gold from the ore.

Outline of Ordinary Modern Practice.—On the Rand the lime required to give the necessary alkalinity is added to the ore before crushing.

Method I. When producing and treating sand and slime.
,, II. When the whole of the ore is slimed.

I. Many ores will give a profitable extraction of their gold without being wholly converted into slime, and although a higher extraction could be obtained by sliming the whole, the cost of fine grinding may be more than the value of the extra yield of gold.

The chief operations are as follows :—

1. Breaking the ore to 1⅜ inches in rock breakers.
2. Crushing in the stamp battery to about ¼ inch.
3. Classification, and dewatering of the pulp, to about 40 per cent. of water, in cones or Dorr classifiers, the slime going to the slime treatment plant, and the coarse to tube mills.
4. Tube milling of the coarse pulp.
5. Amalgamation of the tube mill product on amalgamated plates.
6. Separation of the pulp from the plates into sand and slime by means of cones, sand-filter tables, or other machines, the slime passing to the slime plant.
7. Collection of the sand in collecting vats, more slime being separated. In these it receives a preliminary leaching before being transferred to the treatment vats below. By this transfer the charges are aerated.
8. Leaching in the treatment vats. In some plants the leaching is completed in the collecting vats.
9. The solutions and wash waters containing the gold are run to settling vats, from which when settled they go to the precipitation plant.
10. At the precipitation plant the gold is precipitated in the zinc boxes, or by zinc dust.
11. Treatment of the gold precipitate to convert it into bullion.

II. Treatment when the ore is slimed :—

1. The operations of breaking, crushing, classifying, and dewatering are carried out as described above.
2. Tube milling. The pulp, after being ground in the tube mills and passed over amalgamation plates, is returned to the tube mill classifying cones. The overflow of these cones passes to the slime plant, and the coarse is reground in the tube mills.

The pulp is thus returned to the tube mills until it is slimed—*i.e.*, sufficiently ground to overflow at the cones. This is termed the " closed circuit " system.

3. The slime thus produced goes to settling vats, or to thickening machines, to separate the excess of water it contains.
4. It is then transferred to agitators, where it is agitated with cyanide solution, either mechanically or by air agitation. The chief forms of these agitators are described on pp. 308 to 316.
5. After agitation the pulp is transferred to a stock-pulp vat, and thence to vacuum filters or filter presses. Formerly the gold-bearing solutions were separated by decantation, but this is being given up, and is not practised at the latest plants. The solutions are led to clarifying or sand-filter vats, and the spent residue is sent to the dump.
6. The clear solutions from the clarifiers pass to the precipitation plant (see p. 325).

At some plants, where tube mills have not been installed, the following procedure is practised :—

1. Breaking in rock breakers, as above.
2. Crushing by stamps through 20- to 40-mesh screens.

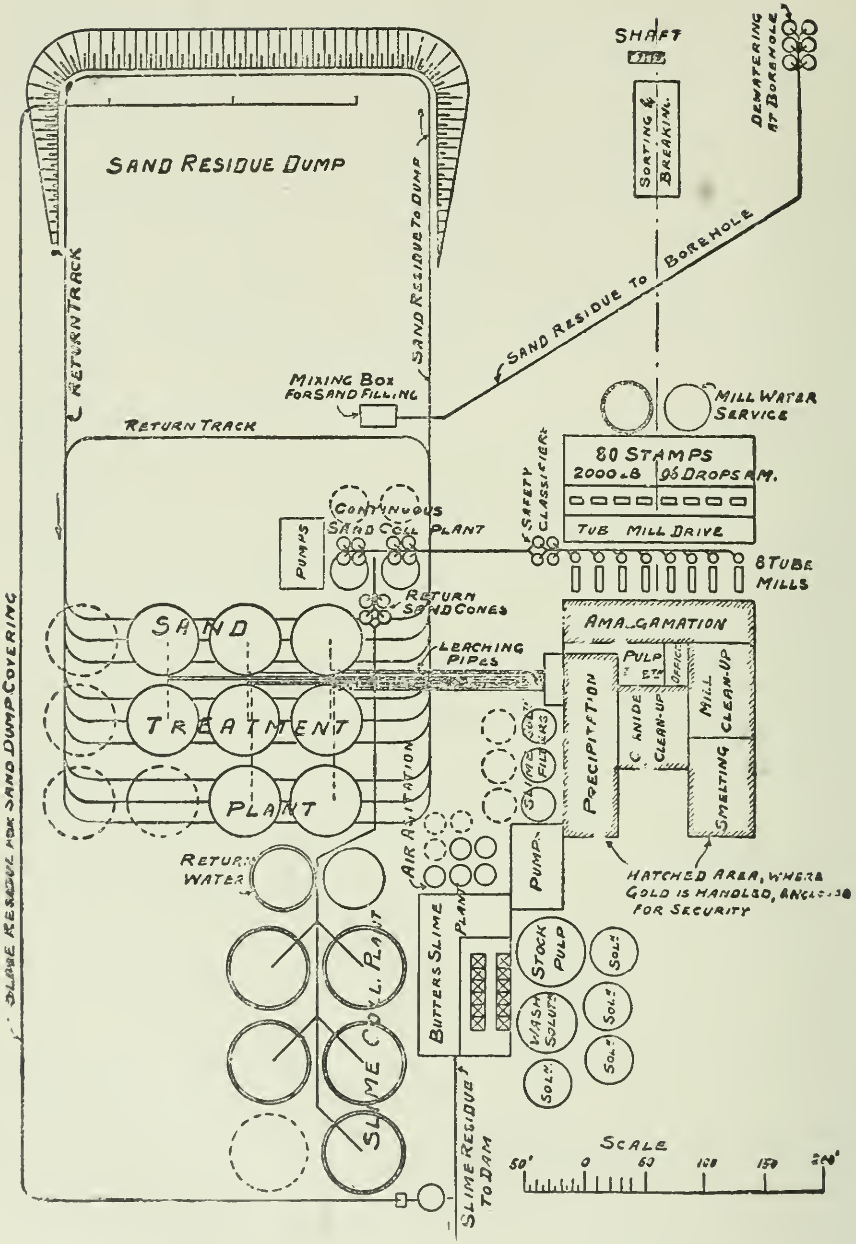
SHAFT
SORTING & BREAKING
DEWATERING AT BOREHOLE
SAND RESIDUE DUMP
RETURN TRACK
SAND RESIDUE TO DUMP
SAND RESIDUE TO BOREHOLE
MIXING BOX FOR SAND FILLING
RETURN TRACK
MILL WATER SERVICE
80 STAMPS
2000 LB
95 DROPS P.M.
TUB MILL DRIVE
SAFETY CLASSIFIERS
8 TUBE MILLS
CONTINUOUS SAND COLL PLANT
PUMPS
RETURN SAND CONES
LEACHING PIPES
SAND TREATMENT PLANT
AMALGAMATION
PULP ETC.
OFFICE
PRECIPITATION
CYANIDE CLEAN-UP
MILL CLEAN-UP
SMELTING
SLIME FILTERS
AIR AGITATION
RETURN WATER
PUMP
HATCHED AREA, WHERE GOLD IS HANDLED, ENCLOSED FOR SECURITY
BUTTERS SLIME PLANT
STOCK PULP
WASH SOLUTION
SOLN
SOLN
SOLN
SOLN
SLIME COLL. PLANT
SLIME RESIDUE TO DAM
SLIME RESIDUE FOR SAND DUMP COVERING
SCALE
50'
0
50
100
150
200'

Fig. 110.—Modern Rand Reduction Plant.

3. Classification of the pulp in a series of diaphragm cones, the slime going to the slime plant, and the sand to the sand plant.

4. In some mills the sand is treated on a sand filter table, to dewater it and further free it from slime before passing to the sand plant.

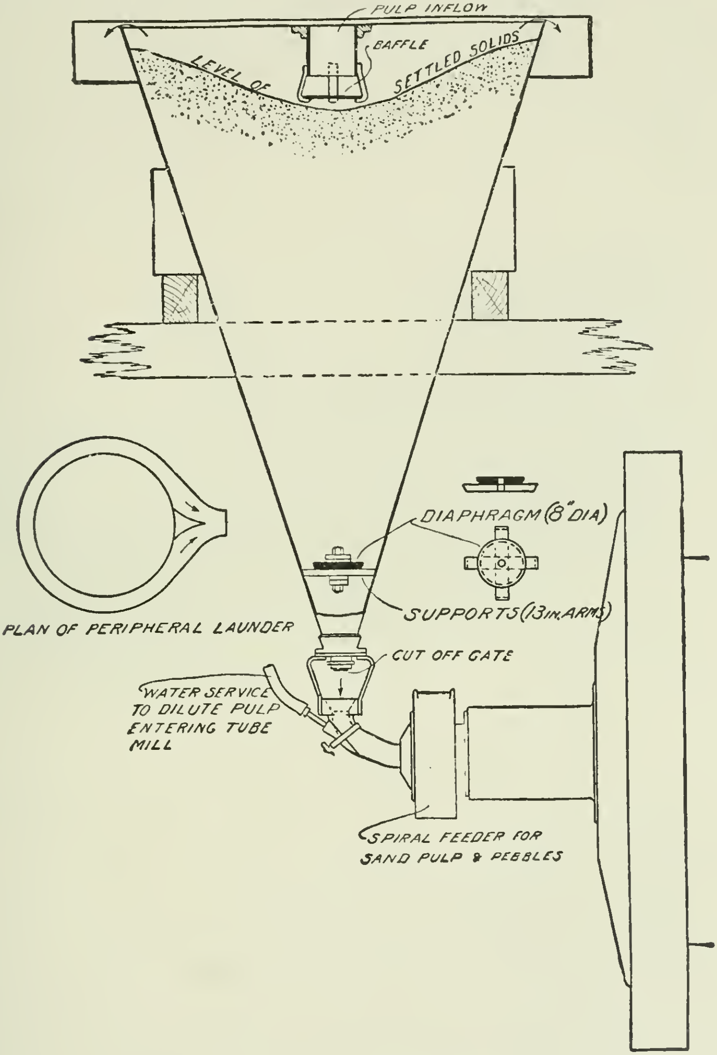
PULP INFLOW
BAFFLE
LEVEL OF SETTLED SOLIDS
DIAPHRAGM (8" DIA)
SUPPORTS (13 IN. ARMS)
PLAN OF PERIPHERAL LAUNDER
CUT OFF GATE
WATER SERVICE TO DILUTE PULP ENTERING TUBE MILL
SPIRAL FEEDER FOR SAND PULP & PEBBLES

Fig. 111.—Tube-Mill Classifier (Cone, 6 feet in diameter by 9 feet deep), with "Caldecott" Diaphragm.

5. At the sand plant the sand is treated as in I., 7, 8, 9, 10, and 11.

A modern Rand Reduction Plant, arranged to provide for future extension, is shown in Fig. 110.

MODERN PLANT AND APPLIANCES EMPLOYED IN THE TREATMENT OF SAND.

The Diaphragm Cone Classifier.—After crushing the ore in the stamp battery it is necessary to separate the slime from the sand, in order that the latter may be leachable, and also be dewatered. The pulp is hence first passed through one or more diaphragm cone classifiers devised by Caldecott. A typical cone is shown in Fig. 111. The cone is of sheet iron, its sides making an angle with each other not exceeding 60°. A standard size in use is 6 feet in diameter by 9 feet deep, with a flat disc diaphragm 8 inches in diameter. Larger cones, 8 feet in diameter by 10 feet deep, with 12-inch diaphragm, are sometimes employed on the Rand when sand-filter tables are in use.

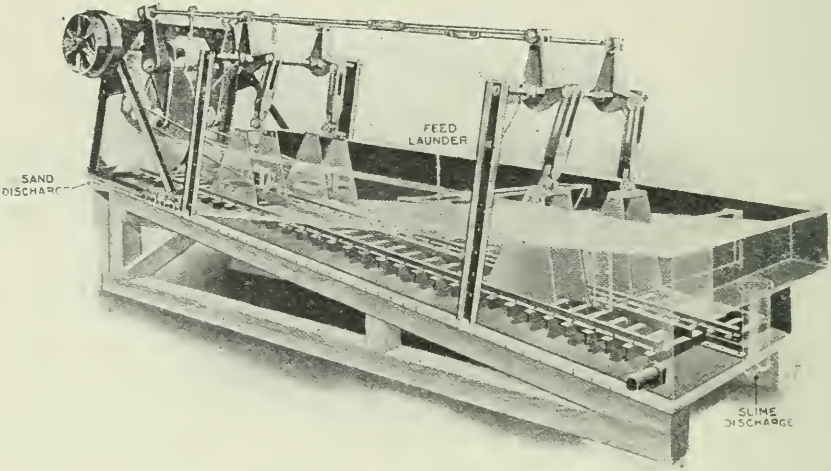

Fig. 112.—Duplex Dorr Classifier *

The diaphragm is fixed, so that its periphery should be about 2½ inches from the side of the cone.

The proper position must, however, be found by experiment.

In some cases two diaphragms of sheet iron are used, the upper being about 2 feet above the lower.

The nozzle at the base is fitted with a sliding shutter, which can be opened and closed as required for regulating the quantity of sand drawn off. The diaphragm is absolutely necessary, as without it the sand has a tendency to rush out, forming a channel, through which the pulp will pass unclassified.

The stream of pulp is fed into the cone through a pipe dipping below the surface of the contents, and having a baffle plate suspended from it to prevent undue disturbance of the sand. By means of treatment in cones of this type only about 5 per cent. of slime will be left in the sand. If it is advisable to still further reduce the proportion of slime, the bottom discharge must be diluted and passed through another cone, after which only about 1 to 1½ per cent. of slime will be left in the sand. The overflow from the cones should also be treated in other cones, to separate any sand which may have passed over, before being led to the slime plant.

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* From block kindly supplied by the Cyanide Plant Supply Company.

The sand from the bottom discharge of the cones flows to a centrifugal pump, by which it is elevated and delivered to collecting vats through a Butters and Mein's distributor, or by means of a hose; or it flows on to a sand-filter table, and is thence transferred to the collecting vats. In tube milling it is delivered to the tube mill, one cone only being required.

Another classifier which has taken a prominent position in Mexican and American practice is the Dorr classifier (Fig. 112).

The Dorr Classifier is a box with an inclined bottom, 15 feet long, 2 feet deep, and 4½ feet wide at the upper by 4 feet wide at the lower end. The grade is 1 inch per foot. Lengthwise in each box are two shafts, each carrying at intervals of 5 inches a toothed scraper blade, 3 inches deep. These scrapers are actuated by a crank, with 10-inch swing, connected to each shaft. The scrapers are drawn forward along the bottom, then raised and pushed back 10 inches, to be drawn forward on the bottom again. The pulp is fed in about one-third of the length above the tailing discharge; the heavier material is scraped out at the head, and the lighter washed out at the tailing end.

By this simple system of reciprocating scrapers working in an inclined trough, Dorr separates the sand up to 200 mesh, or any required degree of fineness, handling about 700 tons of pulp per day with less than ½ H.P.

The Caldecott Sand-Filter Table.—This machine has for its object the continuous collection and dewatering of sand. Collecting vats, as such, are not required, so that the sand may be sent direct to vats for treatment with cyanide.

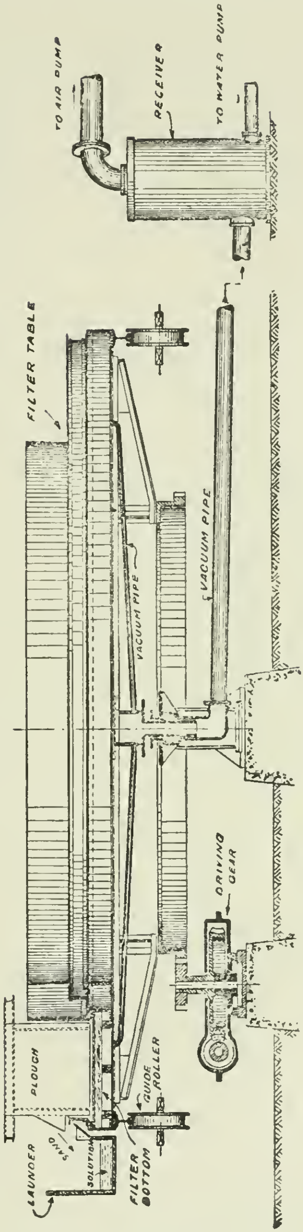

Fig. 113.—Caldecott Sand Filter Table. (*Rand Metallurgical Practice*, vol. i., p. 175.)

The table is shown in Figs. 113 and 114. It is about 20 or 25 feet in

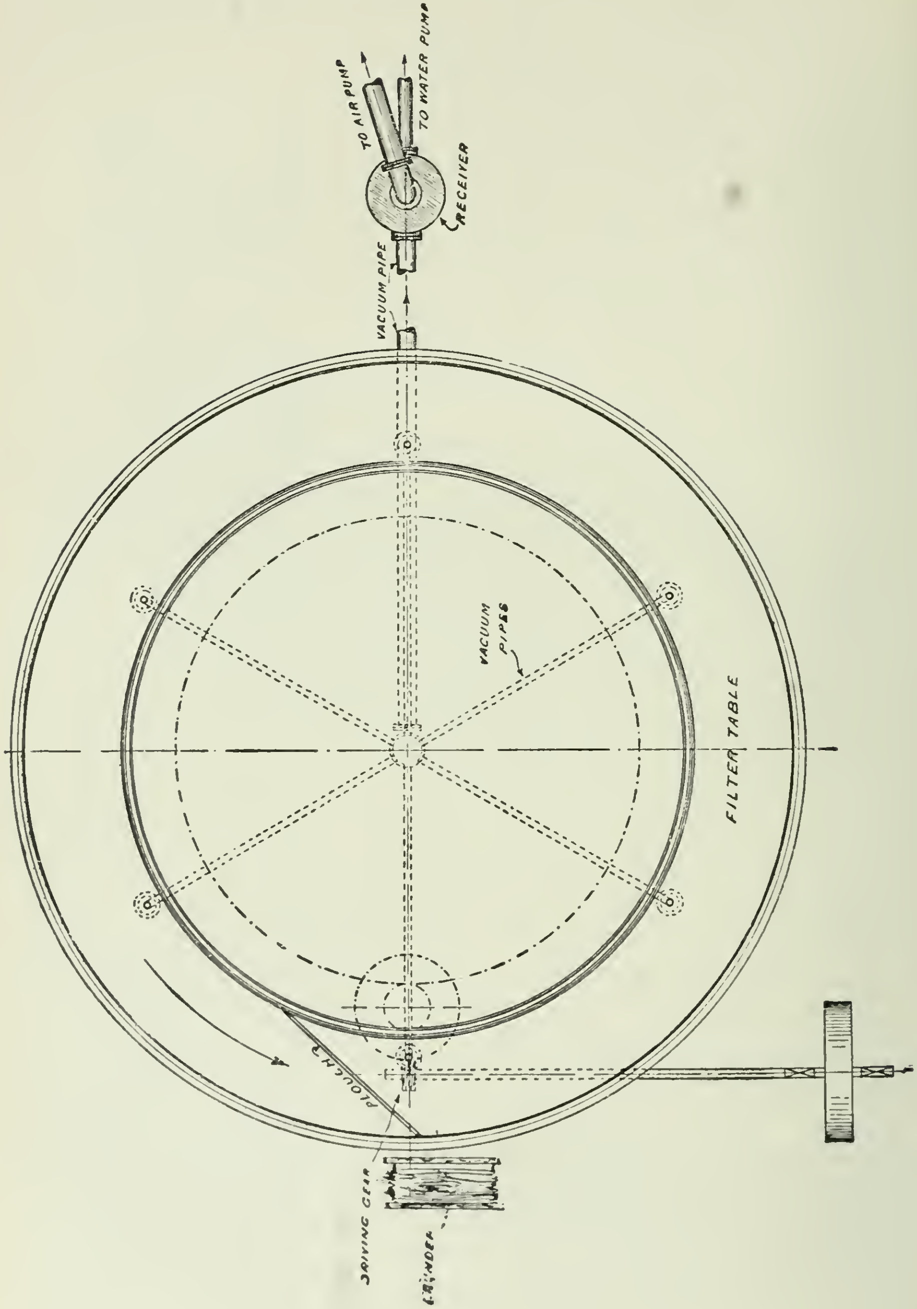
TO AIR PUMP
TO WATER PUMP
RECEIVER
VACUUM PIPE
VACUUM PIPES
FILTER TABLE
PLOUGH
DRIVING GEAR
CYLINDER

Fig. 114.—Caldecott Sand Filter Table (Plan). (*Op. cit.*, vol. ii., p. 229.)

diameter, and consists of an annular launder, in which is fitted a grating carrying the filter. It revolves on guide rollers at a speed of one revolution every three minutes. The bottom and sides of the launder are coated with bitumen, to make them air-tight. The grating is of 9-mesh screening, and is supported by bevelled slats. Upon it is laid a layer of cocoa-nut matting, with a 6-inch strip of jute below it at the edges, and well caulked in. The filter cloth proper consists of strips of unbleached calico simply laid on the matting. A plough, which can be raised or lowered a few inches, is fitted across the launder for the removal of the sand. The space below the filter is connected by pipes with the centre column, from which a vacuum pipe leads to a receiver connected with an air and a water pump.

The plough is set about 1¼ inches above the filter cloth, and the pulp from the classifiers is fed in behind it. The pumps being started, the superfluous moisture is drawn through the filter to the receiver, the dewatered sand being forced over the side of the table into a launder, containing weak KCy solution, from which it passes to a hopper. From the hopper it is transferred to the treatment vat by a pump. The calico has to be removed at least once every 24 hours.

A table, 20 feet diameter, with a 2-foot 6-inch filter bed, will reduce the moisture in 800 tons of sand per 24 hours from 30 to 12 or 14 per cent., and the product is in an ideal form for percolation.

These sand-filter tables have been adopted at the newest plants in S. Africa.

The Tube Mill.—As, generally speaking, an ore when finely ground will give a higher extraction than when in coarser particles, and as tube mills have been found to be most efficient grinders, they have been adopted at all important mills in S. Africa, and generally elsewhere, except in Australia, where grinding pans are in use as well as tube mills.

The grinding is effected by means of flint pebbles, with which they are rather more than half-filled.

A typical tube mill is shown in Fig. 115. They range in size from 3½ to 5½ feet in diameter, and from 13 to 26 feet in length.

The size most popular in America is 18 feet long by 5 feet in diameter.*

Short tube mills, 4 feet to 8 feet in diameter and 6 feet long, are being experimented with, with a view to the more rapid removal of the ground particles, but at present no data as to their performance is available.

On the Rand the standard size is 22 feet in length and 5 feet 6 inches in diameter. At two recently equipped mills, however, the diameter has been increased to 6 feet, and the length shortened to 16 feet. The shell is constructed of ¾-inch steel plates, with welded or butt-riveted joints. There should be no projections inside the cylinder, so that the replaceable lining may be fitted.

The manholes for removing and replacing the pebbles and for relining and repairs should be two in number, and be placed on opposite sides of the cylinder, each half-way between the middle and the end.

The ends are of cast steel with radial ribs.

The sand and pebbles are fed through the feed hollow trunnion, which is 9 inches in internal diameter, and is lined with ½-inch steel. The discharge of the mill is through a hollow trunnion at the opposite end. It is 19 inches in diameter internally, the discharge is thus 5 inches lower than the feed.

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* Rose, *op. cit.*, p. 233.

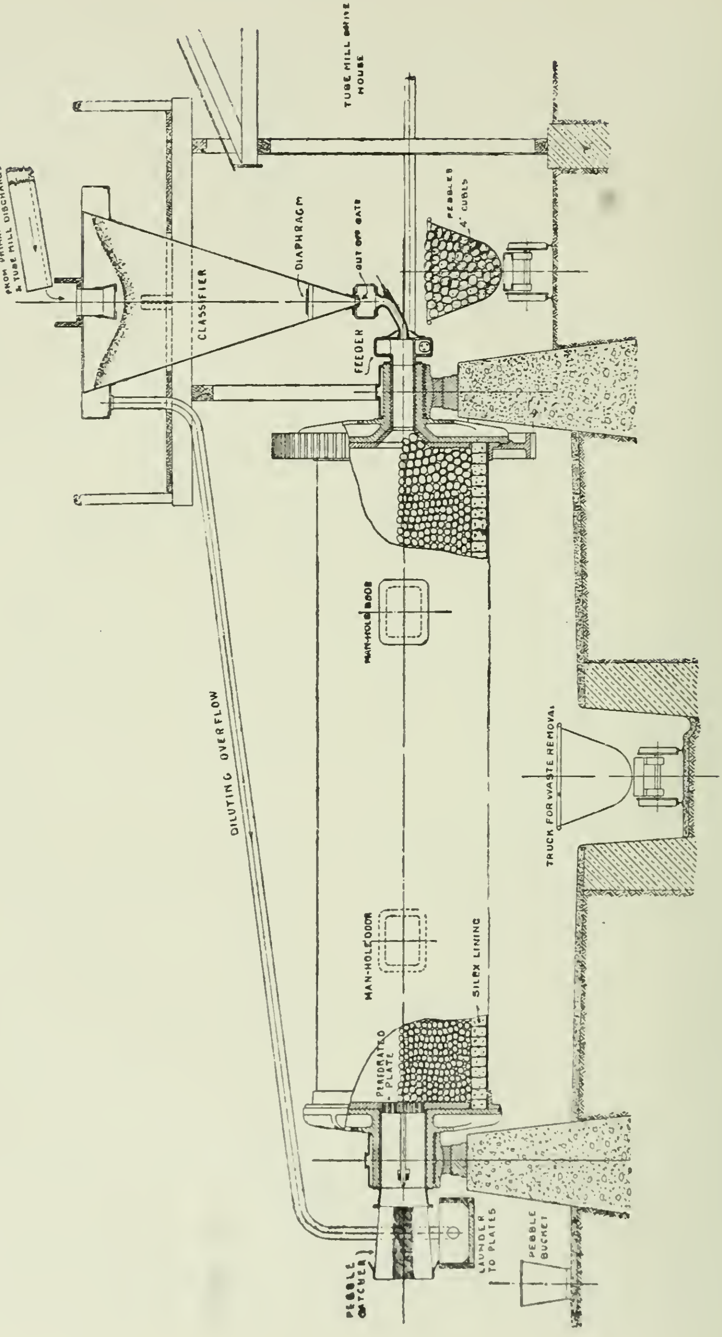
FROM PRIMARY CRUSHING PLANT & TUBE MILL DISCHARGE
CLASSIFIER
DIAPHRAGM
CUT OFF GATE
FEEDER
TUBE MILL DRIVE HOUSE
PEBBLES 4' CUBES
DILUTING OVERFLOW
MAN-HOLE DOOR
MAN-HOLE DOOR
SILEX LINING
TRUCK FOR WASTE REMOVAL
PERFORATED PLATE
PEBBLE CATCHER
LAUNDER TO PLATES
PEBBLE BUCKET

Fig. 115.—Arrangement of Tube Mill and Classifier. (*Op. cit.*, vol. ii., p. 147.)

The cast-steel ends are protected internally by liners, also of cast steel. In some cases the ends are lined with silex or flint blocks. A plate perforated with holes, tapering from $\frac{1}{2}$ to $\frac{3}{4}$ inch, to prevent choking, is fixed at the inner end of the discharge; the pebbles are thus kept back, while the pulp passes out of the mill.

Outside the discharge opening a trommel with $\frac{1}{4}$-inch openings is fixed, to separate the fragments of pebbles which may be discharged with the pulp.

The mill is supported by the trunnions, which run in bearings, and is driven by pinion gear at one end. At some mines the tube mill is supported on tires and friction rollers, but these are said to be more expensive to maintain. Each tube mill of the above dimensions requires about 100 B.H.P for driving.

On the Rand an electric motor of 125 H.P. is generally in use for each mill.

Tube mills are lined in various ways, a common lining being silex or flint blocks, ready dressed in Europe to give a thickness of about 6 to 7 inches, and laid with cement mixed with sand. Recently a local flint or chert has largely replaced the European blocks.

According to Dowling, in a $5\frac{1}{2}$-foot × 22-foot tube mill producing upwards of 100 tons of 90-mesh product per 24 hours, and with fairly coarse battery screening, the life of a 6-inch local chert liner will be about 80 days' actual running time.

Opinion is not unanimous as to the most suitable proportion of tube mills to stamps; at the new plant of the City Deep there is one to every 25 stamps, at the mills of an important group on the Rand one to 15 has been decided on after experiment. The ratio of ten heavy stamps per standard tube mill is, however, the usual modern practice on Rand ore (Rose).* The lining at several mills consists of plates, about $1\frac{1}{4}$ inches in thickness, of chilled cast iron, and in some of manganese steel, bolted to the shell, or keyed on. They are said, however, to wear smooth, then the pebbles skid, and are not lifted sufficiently high.

Several other liners are in use, and various advantages are claimed for each, but whichever is employed, it should be set in such a way that the slip of the pebbles should be as little as possible, or they will not fall from a sufficient height to do satisfactory work.

The chief of these liners are the El Oro, the Osborn, the Komata, and the Honey-comb.

The El Oro Liner consists of a series of parallel ribs of hard cast iron about $3\frac{1}{2}$ inches apart at the top and $3\frac{1}{4}$ inches at the bottom (Fig. 116).

The ribs are tapered in this way, so that the pebbles may not be permanently retained, but may drop out, from time to time, as in the Osborn liner, and be replaced by others, the lining being thus automatically renewed.

The ribs project 3 inches from cast-iron segments, 4 feet long by 1 foot wide, with a base 1 inch thick, which are bolted to the shell of the mill. Replaceable ribs have been proposed for this liner, so that the backing need not be removed when relining is necessary.

The Osborn Liner (Fig. 117) † consists of tapered bars of hard steel placed longitudinally within the shell of the mill and kept at the requisite distance by mild steel bars. In working the mill the space between the bars gradually

* Rose, *The Metallurgy of Gold*, p. 403. † *Ibid.*, p. 235.

fills with pebbles, which take up most of the wear and prolong the life.

The Komata Liner (Fig. 117*a*[*]).—The angle bars which form the ribs of the liner are of manganese steel, the liner plates being either of the same material or of white cast iron or semi-steel. The filler bars, which are placed below the angle bars, are not exposed to wear, and, therefore, are of soft cast iron. The several parts are fixed to the shell by bolts as before. The ribs are spaced 18 inches or 20 inches apart, according to the diameter of the mill, and are not intended to be jammed with pebbles. It is in wide use, having replaced other liners at many plants.

The "Honey-comb" Liner.—The lining of honey-comb blocks is formed of light cast-iron frames, about 22 by 14 by 3½ inches deep, shaped to the curve of the shell, and divided into four or six compartments. Each compartment is firmly packed with rough lumps of hard quartz, or quartzite mine material, bedded in cement. These frames are secured to the shell with cement and locking bars.

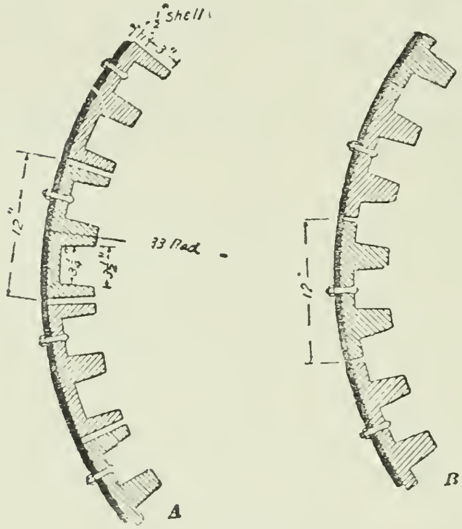

Fig. 116.—El Oro Liner.[†]

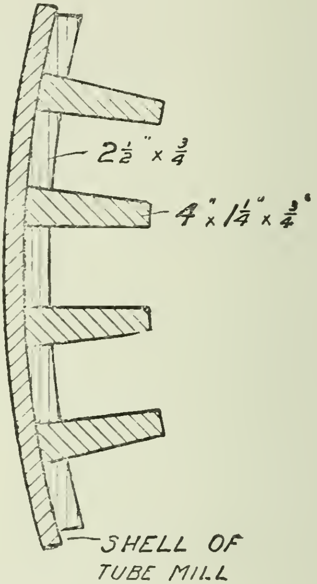

Fig. 117.—Osborn Liner.

The Gibson Liner consists of short ends of drill steel, set in concrete, between which the pebbles lodge.

Rib liners appear to increase the efficiency of the tube mill, and to overcome slip of the pebbles, but also to increase the power consumption. It seems as if they would be more widely adopted.

The pulp and the pebbles are fed into the tube mill by means of various feeders, two of the chief being the Pryce and the Schmitt.

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[*] Rose, *op. cit.*, p. 235. (Reproduced with the permission of the Cyanide Supply Co.)

[†] *Rand Metallurgical Practice*, vol. ii., p. 156.

The Schmitt Feeder (Fig. 118*).—This feeder, which has practically displaced all other devices on the Rand, consists of an outer annular chamber for receiving the material to be fed, and containing a vane or plate for conveying it to the second or inner chamber, which contains a spiral for elevating the material into the trunnion of the mill. In view of the fact that the receiving chamber is always open, it has been rendered possible to adopt mechanical means for handling pebbles—*i.e.*, supplying them mechanically to the feeder. It has the additional advantage that it can receive the pulp at a point below the centre of the tube mill. It can handle pulp of any consistency, and its capacity for feeding pebbles is only limited by the size of the inlet opening of the tube mill.

The Pryce Feeder consists of a hollow casting containing a spiral into the open end of which the pebbles are fed, and pass thence to the inlet of the mill, where their passage is aided by a short Archimedean screw. The pulp is fed in through a central opening in the casting.

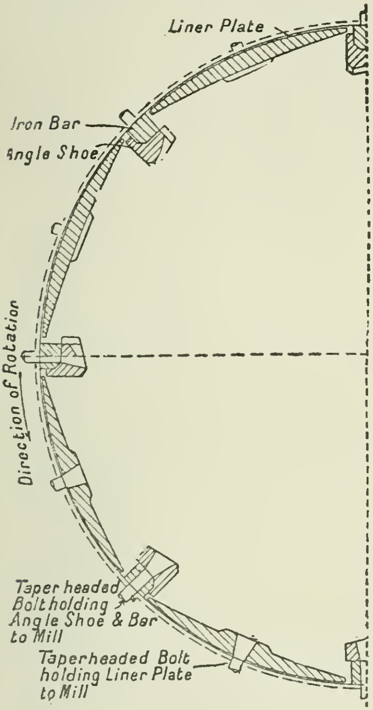
Liner Plate
Iron Bar
Angle Shoe
Direction of Rotation
Taper headed Bolt holding Angle Shoe & Bar to Mill
Taperheaded Bolt holding Liner Plate to Mill

Fig. 117c.—Komata Liner.

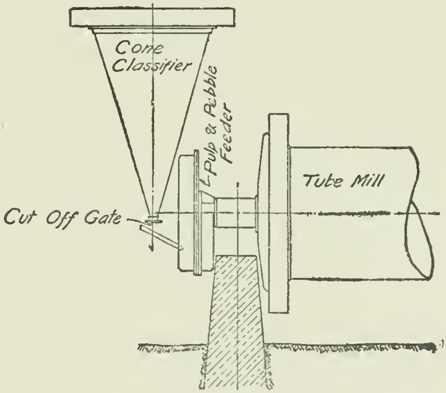
Cone Classifier
Pulp & Pebble Feeder
Tube Mill
Cut Off Gate

Fig. 118—Schmitt Patent Pulp and Pebble Feeder.

Tube Mill Pebbles.—The supply of flint pebbles for the tube mills was an important industry on the coast of Normandy, but Danish pebbles were preferred, although they cost more, as they are said to be more durable. The demand for them, however, has greatly diminished, as selected pieces of ore are now used with success. The pebbles used on the Rand are merely selected pieces of banket ore varying from 3 to 4½ inches in size. The quantity of pebbles required varies with the method of working in use, the original size of the pebbles, and, generally, is directly proportional to the work done.

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* *Rand Metallurgical Practice*, vol. ii., p. 103.

A tube mill, 22 feet by 5 feet 6 inches, will require from 5 to 10 tons of pebbles per 24 hours.

The speed at which tube mills (22 feet by 5 feet 6 inches) are driven on the Rand is about 30 revolutions per minute.

The number of revolutions, however, depends not only on the internal diameter of the mill, but also on the character of the ore fed in, the kind of liner, etc., so that the most effective rate has to be determined by actual trials for each type of ore and mill. As regards the consistence of the pulp fed in, the best results appear to be obtained when it is such that the particles of sand adhere to the pebbles and to the lining, as under these conditions whenever a pebble strikes another there are particles of sand between them to receive the impact.

For large feeds about 40 per cent. of moisture is usual, whilst for small feeds it should be less. The pulverizing action of the tube mill is due to the impact of the falling pebbles, but the grinding action between the pebbles does a certain amount of the work, and the proportion of these will vary with the type of mill, the pebble load, and other conditions.

According to Dowling,* the main rules for the satisfactory running of the tube mills are :—

1. Efficient separation from the pulp leaving the battery of that portion which requires regrinding.
2. As complete a separation as practicable of the water from the pulp entering the mills—*i.e.*, the thickness of the pulp must be carefully regulated.
3. Constant maintenance of a full load of pebbles in the mills.
4. Correct speed of the mills.
5. As high a percentage running time as possible.

Amalgamation Plates for the Tube-Mill Pulp.—The introduction of tube mills for grinding has led to coarse crushing at the stamps, as has already been pointed out, hence amalgamation on battery plates is impossible, owing to the scouring action of the coarse pulp.

Therefore, in order to recover any gold too coarse for the cyanide plant, plates have been introduced for the amalgamation of the tube-mill pulp. In Fig. 119 † is illustrated the arrangement adopted at the Simmer and Jack, and in Fig. 120 † the latest practice in which the overflow from the tube-mill classifying cones is also passed over the amalgamating plates.

The removal of plates from stamp mills has led to the introduction of a separate plate house, the advantages of which are increased running time of the stamps, as they have not to be stopped for dressing the plates, also better amalgamation, as the men in charge can give their whole attention to the amalgamation. The operations, too, can be closely supervised, so that there is less risk of loss by stealing. Although there is no rule for the area of amalgamating plates, it is almost certain that the number and area of plates in common use is unnecessarily large, and when they are placed in a separate plate house the total area may be materially reduced.

At the Randfontein Central the total plates erected amount to 9·6 square feet per stamp unit. Three plates, 12 feet by 5 feet, have now been decided to be ample for each tube-mill, the plates to be stationary, and set at a grade of 18 per cent.

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* *J. C. M. and M. Soc., South Africa*, vol. vi., p. 308.

† W. R. Dowling, *Trans Inst. of Min and Met.*, vol. xx., p. 270, *et seq.*

It has been considered necessary that the plates should shake, but experiments have shown that stationary plates are equally effective. The pulp from the tube mill is too thick to give a satisfactory amalgamation on the plates, it is, therefore, diluted with water, so that it may consist of about 1 of sand to $2\frac{1}{2}$ of water.

The Vats.—These are circular, and are constructed of wood or mild steel.

Large vats are of mild steel, and this material is generally employed, except in Western America and at small plants where wooden vats are common. Wooden vats are made of staves, 3 inches and more thick, and 3-inch bottom planks, braced together with hoops of round bar iron with tightening boxes. The inside is dressed smooth and coated with paraffin paint, or a mixture of asphaltum and coal tar.

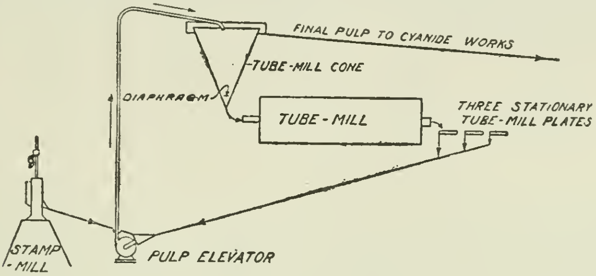
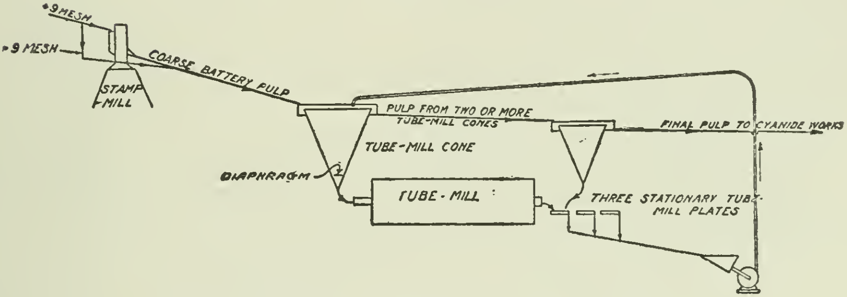

FINAL PULP TO CYANIDE WORKS
TUBE-MILL CONE
DIAPHRAGM
TUBE-MILL
THREE STATIONARY TUBE-MILL PLATES
STAMP-MILL
PULP ELEVATOR

Fig. 119.


9 MESH
9 MESH
STAMP-MILL
COARSE BATTERY PULP
PULP FROM TWO OR MORE TUBE-MILL CONES
FINAL PULP TO CYANIDE WORKS
TUBE-MILL CONE
DIAPHRAGM
TUBE-MILL
THREE STATIONARY TUBE-MILL PLATES

Figs. 119 and 120.— Arrangement of Tube Mill Plates.

The steel vats are built of $\frac{3}{16}$ to $\frac{5}{16}$ inch mild steel plate, single-riveted, with angle irons at the rim and base (Figs. 121 and 122).

The capacity of the vats varies with the character and quantity of the ore or tailing to be treated.

A vat 25 feet by 6 feet will hold about 135 tons.
,, 40 ,, 10 ,, ,, 400 tons.
,, 50 ,, 6 feet at Cripple Creek holds 500 tons.

The depth is determined by the nature of the ore as regards percolation. For dry crushed ore about 4 feet is the limit, while for tailing free from slime the depth may be 8 to 10 or 12 feet. Vacuum and water pumps, working

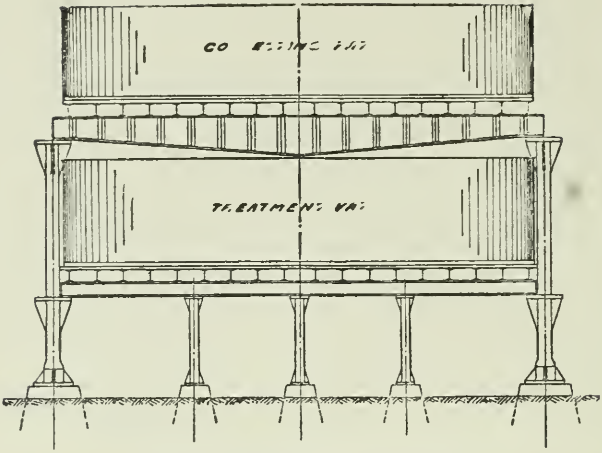

COLLECTING VAT
TREATMENT VAT

Fig. 121.—Cyanide Leaching Vats.*

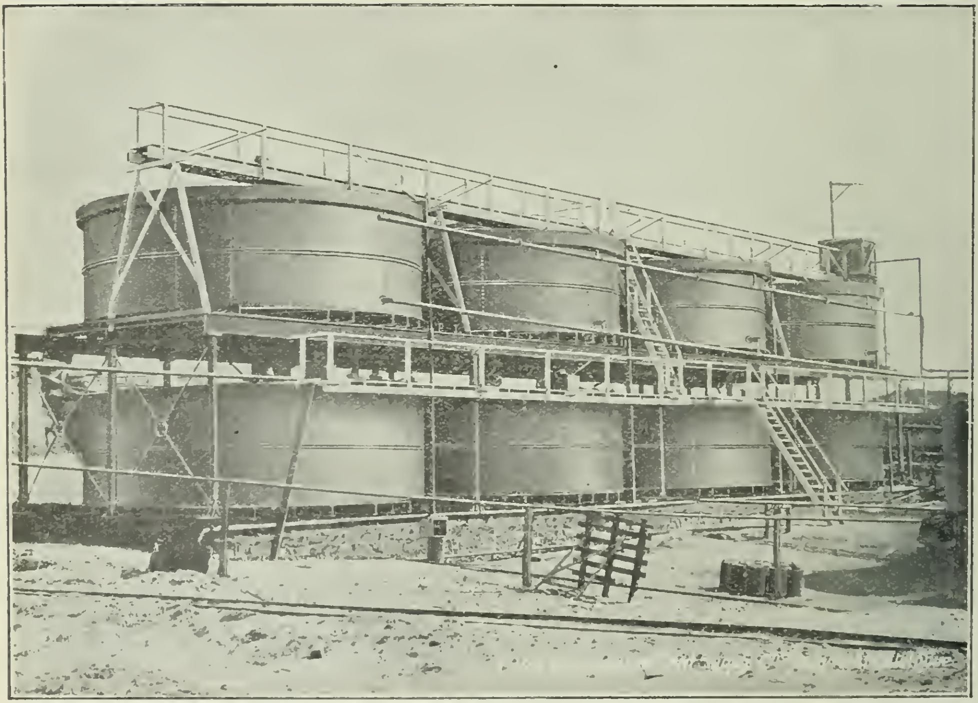


Fig. 122.—Cyanide Vats.†

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* *Rand Metallurgical Practice*, vol. ii., p. 258.
† From block kindly supplied by the Cyanide Plant Supply Company.

on a receiver, usually a large cylinder of boiler plate, are frequently used to hasten percolation, and to aerate the charge.

The filter bottom of a leaching vat is shown in Fig. 123. It is constructed in the following manner :—A ring of wood, about 3 inches high and 2 to 3 inches thick, is fixed to the bottom of the tank, about $1\frac{1}{2}$ inches from the sides.

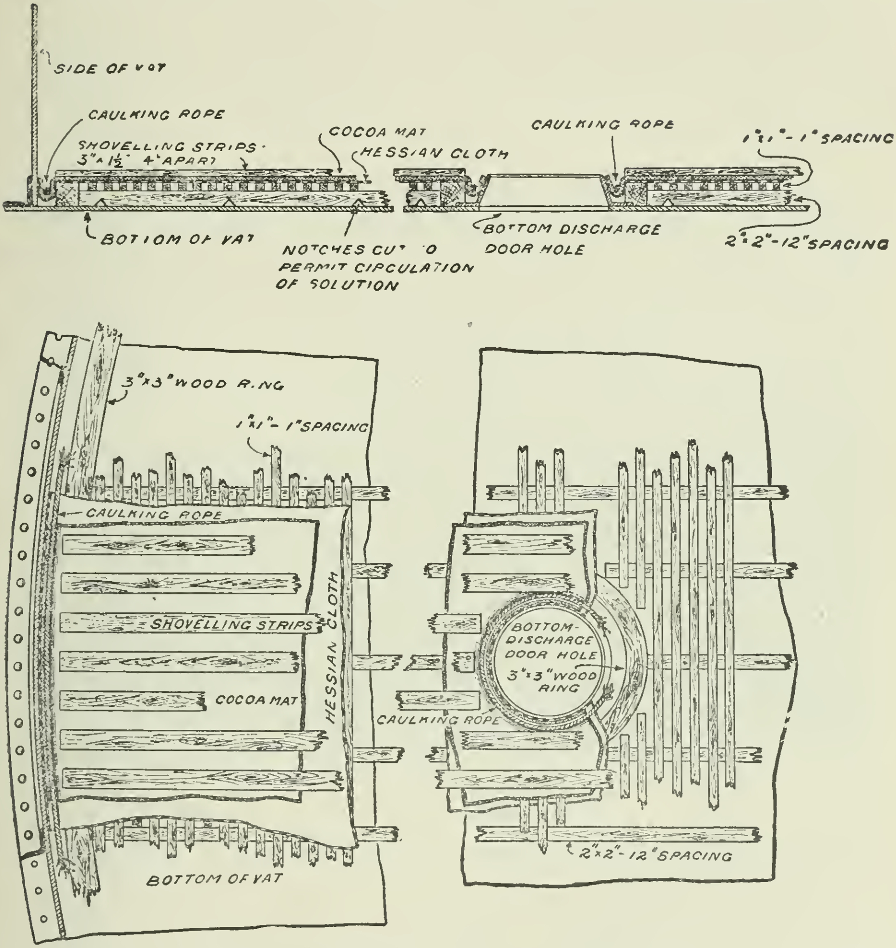
SIDE OF VAT
CAULKING ROPE
SHOVELLING STRIPS 3"×1½" 4" APART
COCOA MAT
HESSIAN CLOTH
CAULKING ROPE
1"×1"-1" SPACING
BOTTOM OF VAT
NOTCHES CUT TO PERMIT CIRCULATION OF SOLUTION
BOTTOM DISCHARGE DOOR HOLE
2"×2"-12" SPACING
3"×3" WOOD RING
1"×1"-1" SPACING
CAULKING ROPE
SHOVELLING STRIPS
COCOA MAT
HESSIAN CLOTH
BOTTOM OF VAT
BOTTOM-DISCHARGE DOOR HOLE
3"×3" WOOD RING
CAULKING ROPE
2"×2"-12" SPACING

Fig. 123.—Construction of Filter Bottom in Sand Vats.*

Within this is a lattice work of crossed slats, in sections convenient for handling, resting on bearers with openings cut in them to allow the solution to flow freely to the outlet pipe. Upon the lattice work is laid either jute matting or canvas, and over this a mat of cocoa fibre.

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* *Rand Metallurgical Practice*, vol. i., p. 159.

The whole is held firmly down by driving in a rope between the ring and the sides of the vat. An open framework of slats is laid over all to protect the filter cloths when the charge is being shovelled out.

In steel vats the filter ring is often of steel riveted to the vat.

The solutions are run off through an iron pipe, which enters the vat below the filter bottom. The pipes and cocks must be of iron, as if of bronze or brass they would be rapidly corroded. The discharge doors in the bottom of the vat are of pressed steel. In small vats there is one in the centre, but in large vats there are several, a 40-foot vat having as many as seven. The spent residue is discharged through them by shovelling, or by a Blaisdell excavator (Fig. 124) into trucks below, or upon travelling belts or conveyors, by which it is taken to the dump.

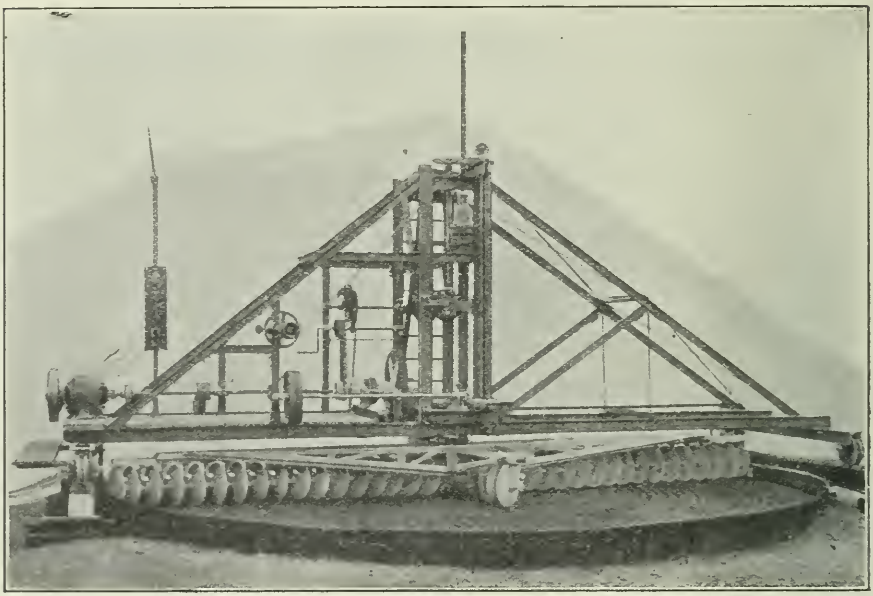

Fig. 124.—Blaisdell Excavator.*

The Collecting Vats.—The object of the collecting vats is to collect the sand and, at the same time, to separate the slime from it, as far as possible. The separation is, however, imperfect, the result being that more or less difficulty often arises in the leaching of the sand. The collecting vat (Fig. 125) is an ordinary leaching vat with filter bottom, but is fitted with an annular launder at the top, into which during working there is a continuous flow of fine slime over the whole rim, the sand settling to the bottom. The vat is first filled with clean water, and the pulp is fed into it from a Butters and Mein's distributor until it is full of sand. When the vat is full the water is drained off, and the sand is either leached in it with cyanide solution in the usual way, or is transferred for leaching to another vat generally placed below. The slime passes to the slime-treatment plant.

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* Julian and Smart, *Cyaniding Gold and Silver Ores*, Fig. 43.

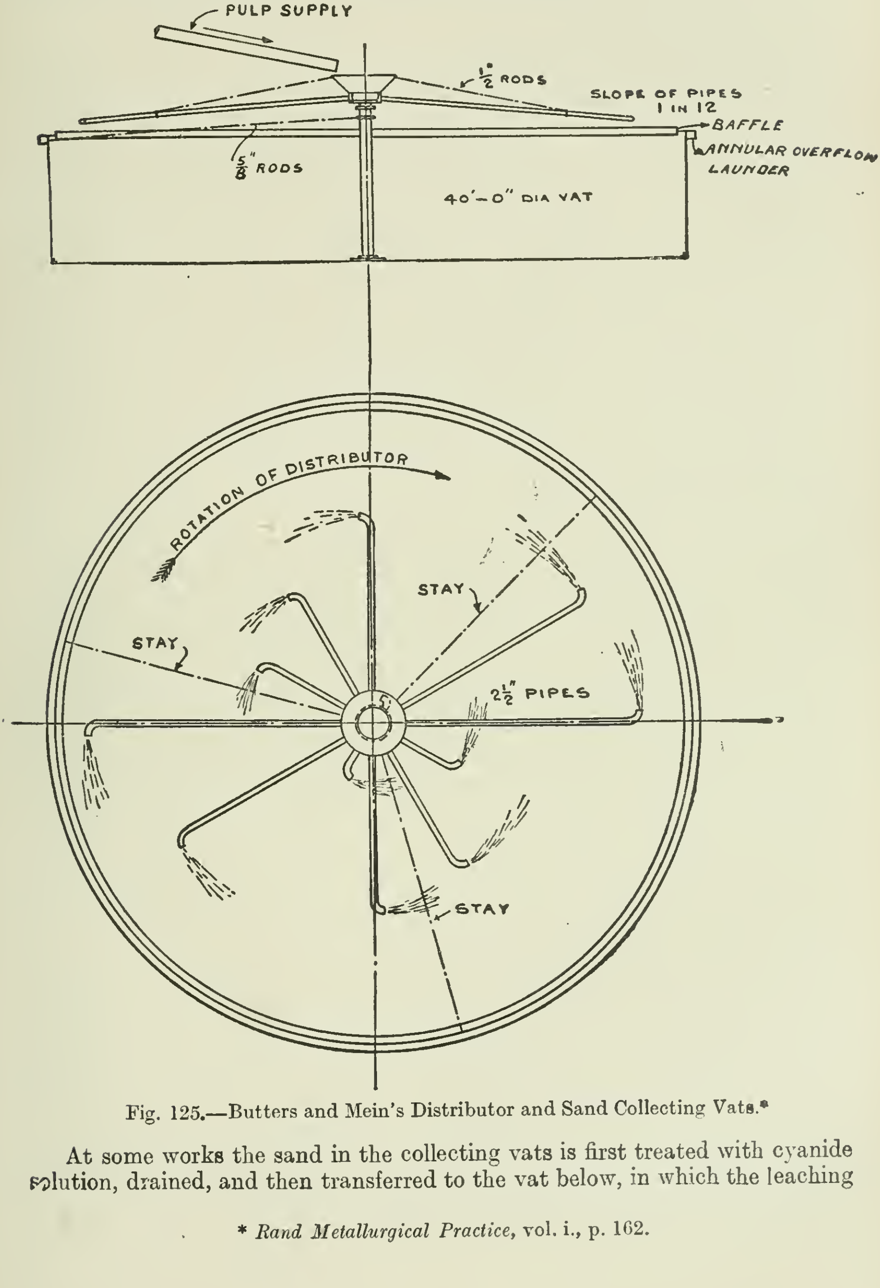
PULP SUPPLY
$\frac{1}{2}$" RODS
SLOPE OF PIPES 1 IN 12
BAFFLE
ANNULAR OVERFLOW LAUNDER
$\frac{5}{8}$" RODS
40'-0" DIA VAT
ROTATION OF DISTRIBUTOR
STAY
STAY
$2\frac{1}{2}$" PIPES
STAY

Fig. 125.—Butters and Mein's Distributor and Sand Collecting Vats.*

At some works the sand in the collecting vats is first treated with cyanide solution, drained, and then transferred to the vat below, in which the leaching is completed. Weaker solutions being used in the former than in the latter. This method is termed "double treatment." The transfer of the sands to a second vat is beneficial to extraction, as the charge is thus not only thoroughly mixed, but also aerated.

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* *Rand Metallurgical Practice,* vol. i., p. 162.

The Butters and Mein's distributor is shown in Fig. 125. It consists of a central hopper with several radial discharge pipes, of varying lengths, with bent ends. The pulp, as it is discharged through these, causes the whole to revolve, and is thus evenly distributed in the vat.

The collecting vats are preferably placed above the treatment vats, for facilitating the transfer of the sand from the former to the latter, otherwise the transfer has to be accomplished by means of trucks or conveyor belts. When they are thus placed they are sometimes supported by columns which pass through the treatment vats; this arrangement, however, is not satisfactory, as the leaching solutions tend to pass down and form channels between the sides of the columns and the sand.

The practice on the Rand of having separate sets of vats for collecting and preliminary leaching the sand, before transference to the treatment vats, will probably be given up, as in one or two of the new mills excellent results have been obtained by the use of a single set of vats.

Further, their special work is being largely performed by cone classifiers and sand-filter tables.

The Blaisdell Excavator (Fig. 124).—This machine has been devised in order that hand labour may be dispensed with and the time of emptying the vats shortened.

It consists of a steel truss bridge supporting in the middle the excavator and driving gear, and at one end the traversing gear and motor for driving. At each end it is supported on trucks, which run on rails laid along the sides of the row of vats, about 3 feet above and 9 inches outside their rims, so that the machine can be traversed and brought over any of the vats. The four excavating arms are carried by a central heavy shaft or spindle supported by the bridge and driven by bevel gearing. To the underside of these arms are bolted cast-iron hangers, each carrying a bearing in which the spindles of the excavator discs revolve. These discs are of thin pressed steel, and are from 20 to 26 inches in diameter. They are set obliquely to the arms, so that they move the sand to the middle of the vat.

The weight of the arms, spindle and discs, etc., is sufficient to force the discs into the sand, but the depth of cut is regulated by feed screws, which are worked automatically. The rate of discharge is governed by their feed. Capacity of the excavator, 50 to 180 tons per hour.

The machine is worked as follows:—The discharge door in the centre of the bottom of the vat having been opened, and a hole dug in the sand immediately above it, the frame carrying the excavating disc is brought into position, and the discs are lowered until they meet the top of the sand. The revolving gear is started, and the required feed set. By the revolution of the arms carrying the discs the sand is forced toward the middle of the vat, and falls through the discharge opening, until the vat is emptied.

The Blaisdell Distributor is employed for the even distribution of the sand in charging the leaching vats. It also has the advantage of breaking up any clots that may be present in the sand.

It consists of a steel truss bridge supporting in the middle a hopper and the distributor. It is traversed from vat to vat in the same way as the Blaisdell excavator.

A revolving vertical spindle passes through the hopper, and has a horizontal steel disc keyed upon the lower end.

Riveted to the upper surface of this disc are short radial vanes of angle iron. The hopper is fed from a travelling belt.

The disc carrying the vanes revolves rapidly, and the sand falling from the hopper upon it is showered evenly over the vat surface below. The machine will throw the sand 25 feet, and hence can be used for vats as large as 50 feet in diameter. By altering the speed of revolution more or less throw can be made, and the shower of sand be passed over the surface of the vat as desired.

Treatment of Sand using a Sand-Filter Table.—The pulp from the crushing plant is first treated by double classification in diaphragm cones for the separation of sand and slime, as it is important, for the efficient working of the sand-filter table, that the sand should contain as little slime as possible. The overflow from the two primary cones is led to a secondary cone, in which any sand present is separated from the slime, the slime then passing to the slime plant.

The plant for carrying out this process is shown in Fig. 126.

The sand from the table may be transferred to the collecting vats, either by means of conveyor belts or in cyanide solution by means of pumps. According to Thomas,* the latter method has the advantage of considerably reducing the time of treatment, owing to the aeration of the sand in contact with cyanide solution during the transfer. "About 60 per cent. of the gold is extracted in the collecting vat, and the remainder of the usual total extraction of 82 to 84 per cent. in the treatment vat."

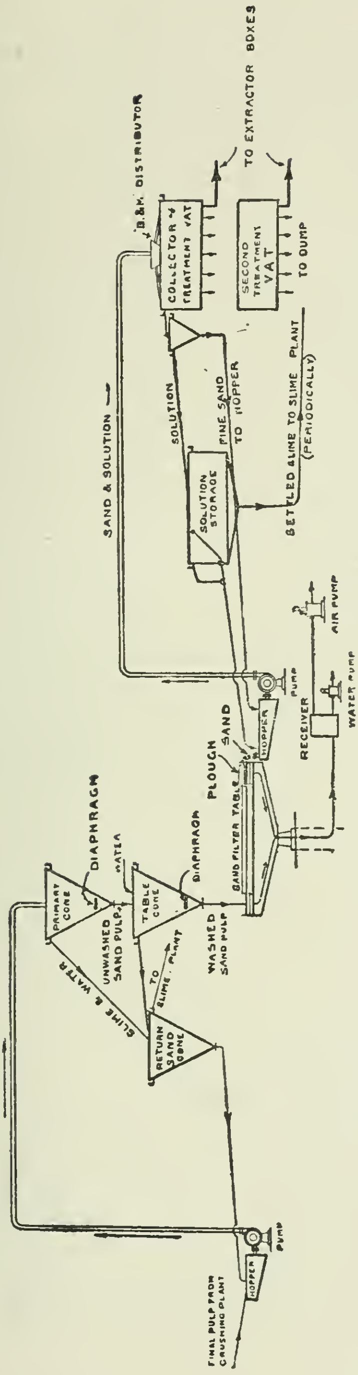
FINAL PULP FROM CRUSHING PLANT
HOPPER
PUMP
PRIMARY CONE
DIAPHRAGM
SLIME & WATER
UNWASHED SAND PULP
WATER
TABLE CONE
DIAPHRAGM
TO SLIME PLANT
RETURN SAND CONE
WASHED SAND PULP
SAND FILTER TABLE
PLOUGH
SAND
HOPPER
PUMP
RECEIVER
WATER PUMP
AIR PUMP
SAND & SOLUTION
SOLUTION STORAGE
SOLUTION
FINE SAND TO HOPPER
SETTLED SLIME TO SLIME PLANT (PERIODICALLY)
COLLECTOR & TREATMENT VAT
B.&M. DISTRIBUTOR
SECOND TREATMENT VAT
TO DUMP
TO EXTRACTOR BOXES

Fig. 126.—Sand Filter with Superposed Cones, etc (*Rand Met. Practice*, vol. i., Fig. 85, p. 177).

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* *Op. cit.*, p 176.

If the treatment is carried on and completed in the collecting vat about nine days are required for a satisfactory extraction. The same result may be obtained in about six days, if the charge is leached dry in the collecting vat and transferred to a second vat for completion of the treatment.

The operations carried out with double treatment are as follows :—

The sand from the filter table falls into a launder containing cyanide solution of 0·025 strength, by which it is carried to the pump.

The collecting vat is filled with precipitated solution of the same strength before the sand is pumped up to it.

The peripheral launder, which receives the overflow from the vat, is fitted with two pipes, so arranged that any sand which has been carried over from the vat is led by one of them to the sand-filter table, and the solution, carrying only a little slime to a storage vat for its settlement and subsequent transfer to the slime plant.

After the filling has proceeded for from two to three hours the solution, which will contain 3 to 4 dwts. of gold, is allowed to drain through the cock at the bottom of the vat to the zinc boxes.

When the vat has been filled with sand, more solution is pumped on from the storage vat, its strength being kept right by the addition of cyanide. At this point lead acetate and, when necessary, lime is also added.

The charge is then leached dry and transferred to the treatment vat in the usual manner. It is then treated with about 15 per cent. of its weight of strong solution, containing about 0·12 per cent. of KCy. It is then leached dry and weak solution 0·05 per cent. KCy run on, after which it is again leached dry, and this treatment is continued until the gold has been extracted, as much as possible. In order that the last drainings should carry off not more than about 0·1 dwt. of gold per ton, the ratio of solution to ore will be about 1·6 to 1·0. For a modification of this method of leaching, see p. 304.

After the leaching and washing of the sand is completed, it is discharged through the doors in the bottom of the vat into trucks, or on to the conveyor belts, by which it is carried to the dump, as already described.

Recently another method of disposing of the residue has been introduced at some mines. The residue is dewatered in cones and run into the old workings of the mine to prevent subsidences. In such cases the residue must be as free as possible from cyanide.

In order to guard against the lowering of free cyanide into the workings, tests are carried out, from time to time, and potassium permanganate is fed into the pulp as a neutralizing agent.

Treatment of Sand when only Cones are in use and the Sand is delivered direct to Collecting Vats.—The ordinary plant consists of a series of vats, which vary in size from 25 to 50 feet or more in diameter, in depth from about 6 to 9 feet, and in number according to the quantity of pulp to be treated. The plant employed at some mines in S. Africa is shown in Fig. 127, from which it will be seen that the system of cone classification is more elaborate than when sand-filter tables are used. There are, as will be seen in the figure, three sets of cones—viz., primary, secondary, and return. The overflow from the two first sets passes to the third, the overflow from which goes to the slime plant, and the underflow to the sand elevator. The underflow from the primary cones is led to the secondary cones, and the underflow from these to the sand elevator. The sand elevator is a centrifugal pump,

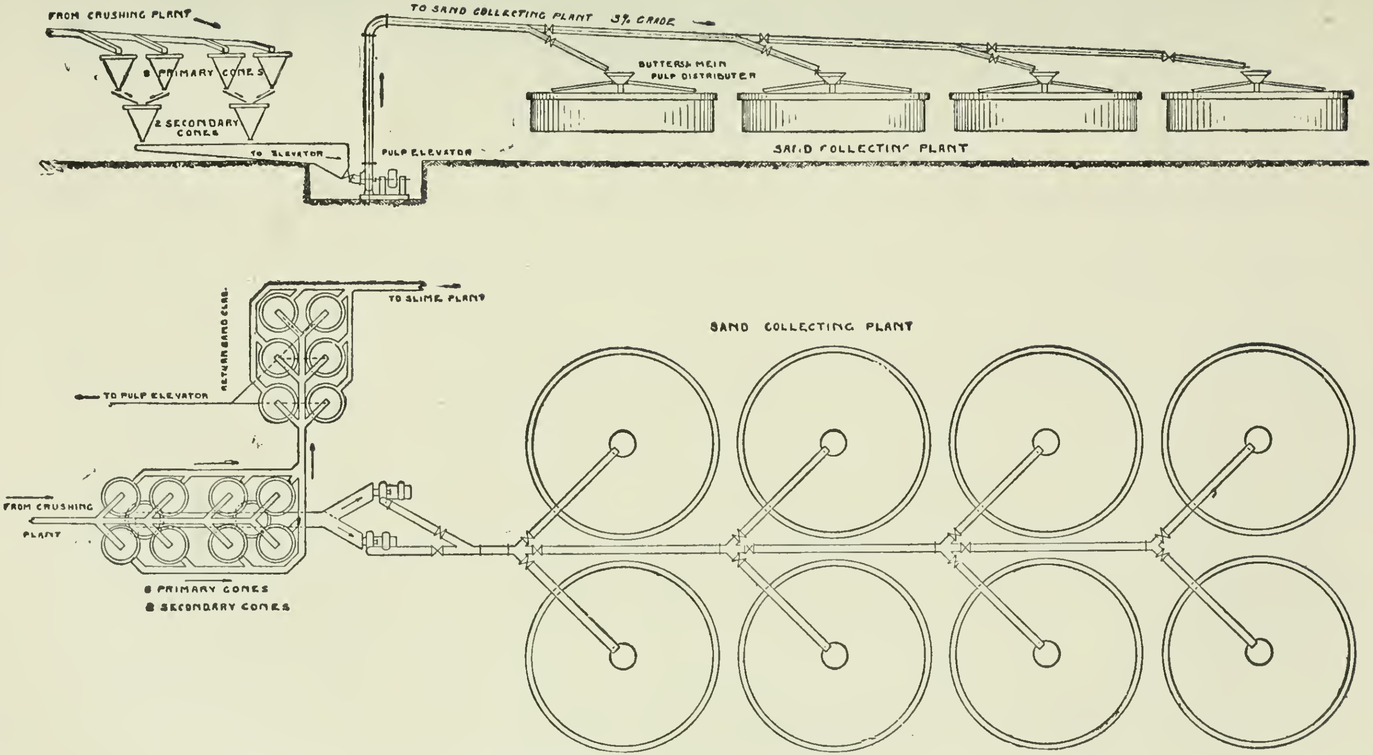
FROM CRUSHING PLANT
8 PRIMARY CONES
2 SECONDARY CONES
TO ELEVATOR
PULP ELEVATOR
TO SAND COLLECTING PLANT 3% GRADE
BUTTERS & MEIN PULP DISTRIBUTER
SAND COLLECTING PLANT
RETURN SAND CLAS.
TO SLIME PLANT
TO PULP ELEVATOR
SAND COLLECTING PLANT
FROM CRUSHING PLANT
8 PRIMARY CONES
8 SECONDARY CONES

Fig. 127.—Double Cone Classification Plant with Return Sand Cones. (*Op. cit.*, vol. i., p. 156.)

and by it the sand is pumped to Butters and Mein's distributors, which feed the collecting vats, the vats being first filled with water.

Each collecting vat is provided with an annular launder, as usual, to receive the overflow of slime and water which then runs to the slime plant. When a vat is full of sand, the water is allowed to run off through the opening below the filter, and when it no longer flows freely its discharge is accelerated by water pumps and vacuum pumps.

As soon as the charge has been drained dry it is often sprinkled with a solution of lead acetate, and is then transferred to a treatment vat.

Several arrangements are in use for the transference of the sand. The best is to have the collecting vats arranged above the treatment vats, as has already been pointed out.

When the vats are all on the same level the sand has to be discharged upon conveyor belts, or into trucks, and elevated to the treatment vats, requiring much labour.

The treatment vats are of greater depth than the collecting vats, but this should not exceed 10 feet.

When, as in modern practice, lime has been added to the ore before crushing, it is not often required at this stage.

Preliminary alkaline washes are hence not required, and the strong cyanide solution may be run on as soon as the charge has been levelled.

Cyanide solution, containing 0·12 of KCy and about 25 to 30 per cent. of the weight of the charge, is usually sufficient.

According to J. E. Thomas, sufficient solution "should be pumped on to the charge to cover it to about a foot in depth, and as fast as this solution leaches down, to follow with more until the desired quantity has been added. The gold-bearing solution is run to the precipitation department."

The charge should then be allowed to drain dry before solution of a different strength is added. The drying should be aided and supplemented by utilizing a water pump to draw off the solution quickly, and air is then drawn through the charge by means of a vacuum pump. When as much aeration has been given as the time available allows, the charge is covered with a weak solution of from 0·02 to 0·03 per cent. KCy, and followed with more until from 30 to 40 per cent. of the weight of the charge has been pumped on. The process of leaching dry and aerating should then be repeated and followed with a further lot of solution of the same strength until from 100 to 140 per cent. of the weight of the charge has percolated to the precipitation plant.

A final wash of solution carrying only a small percentage of KCy should then be applied, after thoroughly draining the charge of the previous solution, and the final draining prior to discharging to the residue dump given. The final solution should preferably be precipitated solution from the slime plant, but if none is available water may be used.

It will usually be found that the ratio of solution to sand of 2 to 1 by weight is ample to dissolve and wash the gold from sand collected and treated in the manner described. The strong and weak solutions from the vats go to their respective zinc boxes for precipitation of the gold, and the spent residue is sent to the dump.

SLIME.

The term slime has not been satisfactorily defined. According to one definition it is that portion of crushed ore which, owing to its minutely subdivided condition and the presence of colloidal substances, settles very slowly in water, and cannot be leached without extra pressure. But generally in practice any portion of ore which is in such a fine state of division that it will pass a 200-mesh screen with 0·003-inch aperture is regarded and treated as slime. It is in the treatment of slime and fine pulp that the chief advances in the cyanide process have been made during recent years.

The decantation process, which originated in South Africa, and which has been in extensive use there, has had its day, and is being gradually superseded by one or other of the methods to be described later.

These methods all deal with the agitation and filtration of the pulp, and for these purposes several forms of plant and apparatus have been designed, the aim of each being to effect these objects, as far as possible, with the least expenditure of power.

The treatment of slime by ordinary decantation hence only requires a brief description.

The Decantation Process.—It is important that the sand should be separated as much as possible from the slime, as the time given in the slime treatment is too short for the solution of the gold in the particles of sand. Moreover, the life of the pumps, used in the transfers of the slime, is considerably shortened owing to the abrasive action of the sand. This separation is effected in modern practice by diaphragm cones, which have already been described (Fig. 111, p. 285), the sand being returned to the sand plant.

The stream of slime from the cones now receives an addition of lime before entering the collector. There are many ways of adding the lime, one of the best being to use a grinding pan, into which the lime is added from time to time as required. It is carried away by a small stream of water as milk of lime direct to the stream of slime. The amount of lime added varies considerably, as some is added in the stamp battery, but usually for pyritic banket it is about 6 lbs. of lime per ton of slime.

The collector is a vat with a conical bottom, about 50 feet in diameter, in large plants. It is fitted with an annular launder to receive and carry off the peripheral overflow of clear water.

The stream of slime pulp is fed into the centre of the collector by a launder and delivery pipe until it is full, and by which time the slime will have settled and clear water overflows. Care must be taken to adjust the inflow of slime, so that settlement may take place before the vat is full.

When the collector has received its full charge, the supernatant water is removed by a "decanter" (Fig. 128). This consists of a hinged pipe that passes through the side of the vat, and by means of the hinge its inlet can be kept just below the surface of the clear water. After the clear water has been thus removed the settled slime is sluiced out with cyanide solution to a pump, by which it is transferred to another vat, the "first-treatment vat." The delivery from the pump is set tangentially to the receiving vat, in order to cause a rotary motion of the pulp and keep it in suspension.

In this vat the charge is circulated by means of another pump, or in some cases is pumped back into the collector vat and returned to this "first-treatment vat." Time required, about four to six hours.

The slime is now allowed to settle and, during settlement, the clear solution called the "first wash" is removed by the decanter, and after passing through a clarifier (see p. 325) is led to the zinc boxes. The strength of the cyanide solution ranges from 0·005 to 0·02 per cent. KCy. A little slime always passes off with the decanted solution, and as this would tend to coat the zinc in the zinc boxes, it must be removed in the clarifiers or by passing the solution through a filter press.

As soon as the first wash has been decanted, the slime is diluted with solution, which has been precipitated, and transferred in the manner already described into the second treatment vat, in which, after a short circulation, it is allowed to settle. The solution is then decanted; it is, however, not sent to the zinc boxes, but is used in transferring the slime from the collector vat to the first settlement vat. The settled slime after dilution with water is then discharged into the slime dam.

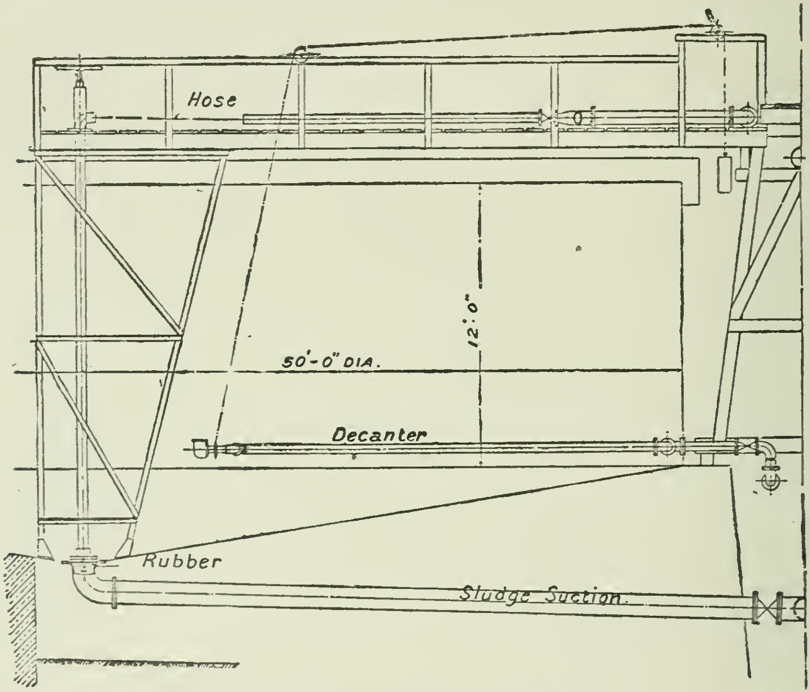

Fig. 128.—Vat with Decanter.*

As in this method of treating slime the time of settlement is considerably shortened, and the gold is more perfectly precipitated in the zinc boxes, if the solutions are hot; if waste steam is available, it is profitable to use

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[*] *Op. cit.*, vol. i., p. 217.

it for heating them, but it is doubtful whether a special plant for heating would pay.

"*Counter-current Decantation.*"—For a description and example of the new method of continuous decantation called "counter-current" decantation, see Porcupine Crown Mill, p. 347.

MODERN PLANT AND APPLIANCES EMPLOYED IN THE TREATMENT OF SLIME.

The most important appliances are :—

(1) Diaphragm cones or other classifiers.
(2) Tube mills.
(3) Pulp thickeners.
(4) Agitators.
(5) Vacuum filters.
(6) Filter presses.
(7) Clarifying vats.
(8) Precipitation plant as for sand.

(1) and (2) **Diaphragm Cones, Dorr Classifiers, and Tube Mills have been** already described on pp. 286 to 294. The function of the first, in the treatment of slime, is to prepare the battery pulp for the tube mills.

The pulp or tailing from the stamp mill will have passed through battery screens of 9-mesh to the square inch, the size of the particles ranging from 0·27 inch downwards; it is hence necessary before it is fed into the tube mill that it should pass through one or more classifiers to separate the coarse particles from those which are already fine enough, also to separate the excess of water in the pulp, to give it the consistence required by the tube mill.

(3) **Pulp Thickeners.**—Before the treatment of slime in agitators, it is necessary that it should be dewatered or thickened, so that the proportion of solution to slime should be as 1 to 1, $1\frac{1}{2}$ to 1, or 2 to 1.

For this purpose a dewatering appliance is employed, and one which is being largely adopted is the *Dorr continuous thickener* (Fig. 129*a*).

It consists of a vat about 25 to 35 feet in diameter, and from 10 to 12 feet in depth, in which a vertical shaft reaching nearly to the bottom, and carrying four arms, slowly revolves. Pieces of angle iron attached to the arms are so placed that they move the settled thickened pulp to the centre of the bottom of the vat, where it is discharged through a pipe. The thin pulp flows into the tank at the centre, considerably below the surface, and the clear liquor overflows continuously at the periphery. It is claimed for this machine that, if the dehydration is continuous, the pulp is reduced from about 10 of water to 1 of dry slime to $1\frac{1}{2}$ of water to 1 of dry slime, whilst if worked intermittently an output of 1 of water to 1 of dry slime is obtained.

The Dorr Tray Thickener.—Fig. 129 is an improved form of the above, and is designed to give a large settling area in a comparatively small space by the introduction of one or more trays. They are built up to 50 feet in diameter, and as many trays can be installed as depth will permit. The tray also provides a convenient and inexpensive means for increasing the capacity of the above *thickeners* where already installed. Comparatively small depth is required for the tray, and the majority of thickeners now in use have sufficient depth for the addition of one tray.

For settling flotation concentrate the tray thickener has a decided advantage in that the froth is confined to the surface of the upper tray only where it can readily be controlled if persistent.

In many plants on the Rand the slime is still thickened by collecting it in settling vats with conical bottoms, a peripheral overflow, and a decanting device for removing supernatant water.

(4) **Agitators.**—The agitation of the thickened slime was usually effected in flat- or conical-bottomed vats by centrifugal pumps, mechanically driven screw-propeller blades, or arm agitators. When centrifugal pumps were used the charge was drawn from the bottom of a vat and delivered over the top of it.

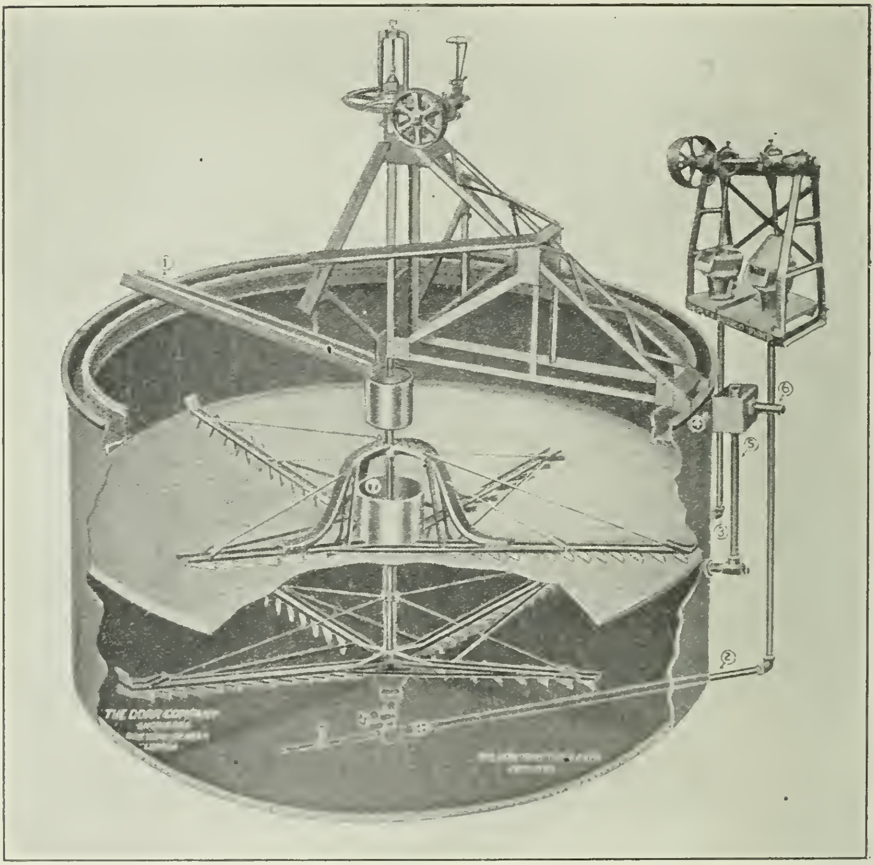

Fig. 129.—Dorr Tray Thickener.

1. Combined Feed.
2. Thickener discharge, lower compartment.
3. ,, ,, upper ,,
4. Clear overflow, upper compartment.
5. Clear overflow, lower compartment.
6. Combined clear overflow.
7. Feed passage to lower compartment.

In the latest plants, however, one or other of the following types of agitation vats have been adopted :—

The Brown (or as it is sometimes called the Pachuca) vat.
The Parral vat.
The Trent vat.
The Hendryx agitator.
The Dorr agitator.
The Just agitator.

The Brown or Pachuca Vat.—Since the invention of this vat by Brown in New Zealand all the large mills in Pachuca (Mexico), and several on the Rand and elsewhere have been provided with these agitators. In this type of vat the agitation is effected by lessening the specific gravity of a central column of pulp, by the introduction of air at just such a pressure as will overcome the pressure of the column at the point of introduction.

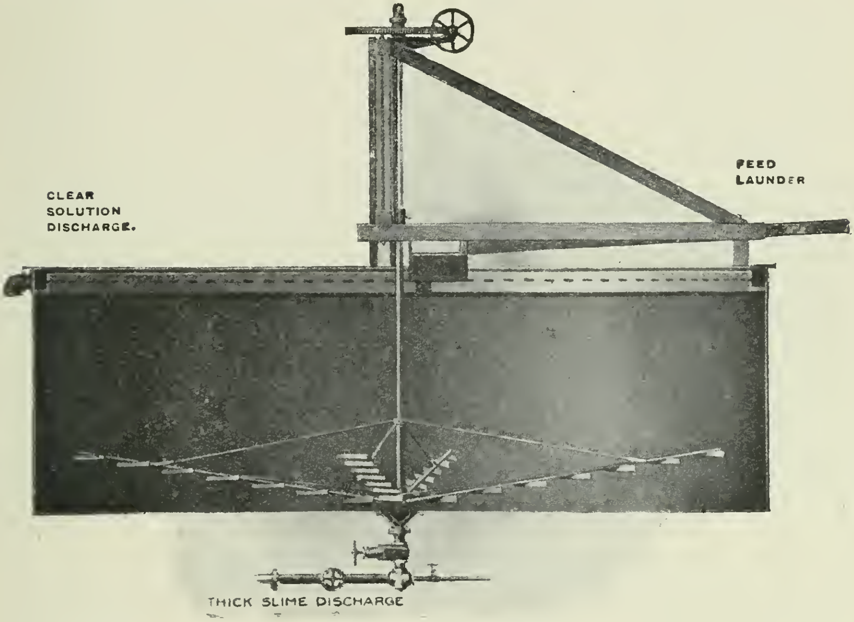

Fig. 129*a.*—Dorr Continuous Thickener.

In Fig. 130* is shown a vertical section of a Brown vat. It consists of a tall cylinder of much greater height than breadth.

B is the central tube, down which passes the internal pipe through which air is forced in. This pipe is fitted with a rubber valve at its lower end. The air bubbling up B carries the pulp with it. An external air pipe C, also with a rubber valve, is used to keep the pulp in motion during the filling or discharge of the vat. The pipe E is used for supplying solution, water, or air to the distributor F, which discharges through the pipes I, I, to prevent packing before agitation is started and when it is stopped.

Air is supplied to the pipes C, D, and E from pipe O, and water or solution from pipe N.

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* F. C. Brown, *Min. and Sc. Press*, Sept. 1908.

An adjustable splash plate Q is fitted near the top of the central tube.

The slime pulp is fed in through the pipe P. The discharge after agitation takes place through pipe K.

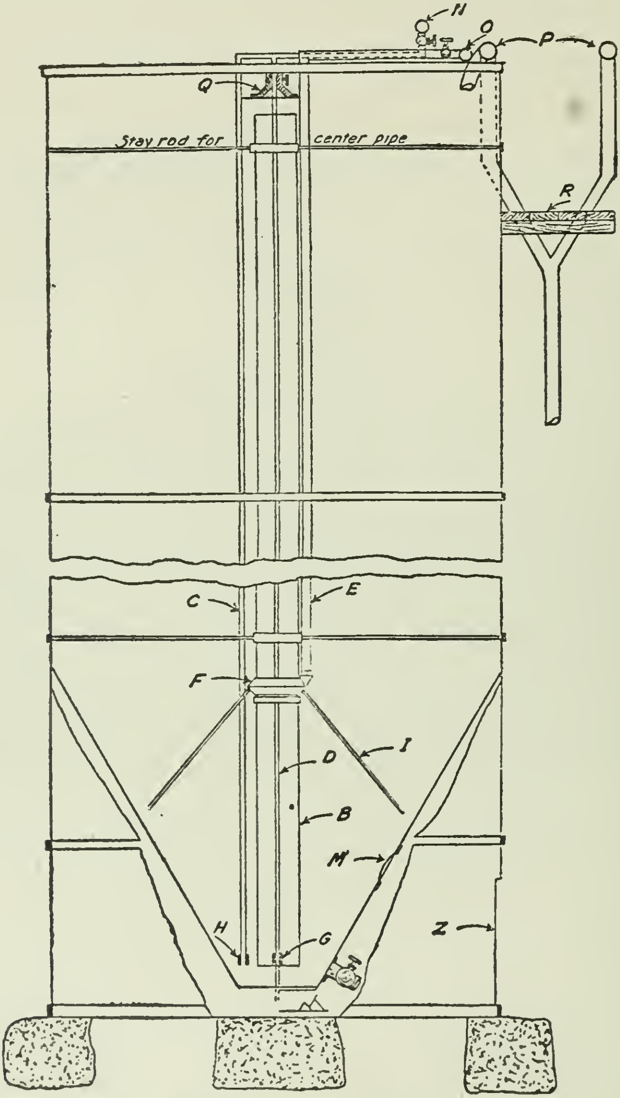

Fig. 130.—Brown Agitator.

These vats are of various sizes, one in common use being 45 feet in height, 15 feet in diameter, and holding about 100 tons of dry slime.

The method of working is very simple. As soon as the tank is filled with slime and solution, air is turned on in the pipe D, and mixing with the pulp in the central tube lightens the column inside, and causes it to overflow, fresh pulp being drawn in at the bottom, producing a perfect circulation.

If the pulp settles, or packs at the bottom, solution, or air, or a mixture of both, is forced in through the pipes I, I. At first the air pressure required is considerable, as it has to overcome that of the column, but when circulation has been established it can be much reduced.

The circulation need not be violent ; it is only necessary to keep all the pulp in constant agitation ; therefore, there should be a proper adjustment of the amount of air blown in.

The usual arrangement of the vats at Waihi, New Zealand, is shown in Fig. 131.

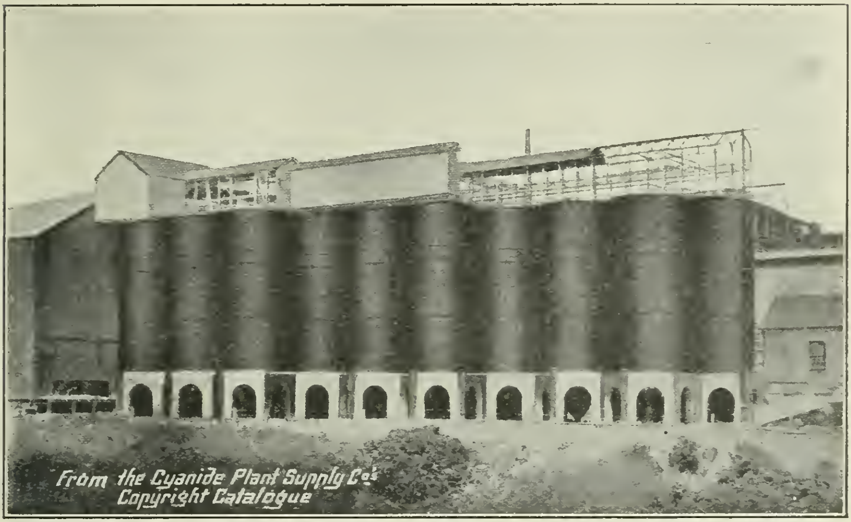
From the Cyanide Plant Supply Co's Copyright Catalogue

Fig. 131.—Brown Agitators at the Waihi Mine, New Zealand.

When the pulp becomes packed at the bottom of the vat, it is brought into agitation, within 15 minutes, at the Treadwell Mines,* Alaska, by a device designated as the "Spider," which is an adjustable hollow annular casting with radiating hollow fingers, the whole encircling the central agitation column.

When the charge is to be put into agitation the spider is lowered by a small hand windlass until it rests on the top of the settled charge. Air is then turned through the fingers, and, at the same time, the slime for the next treatment is run into the vat. The device rapidly bores its way to the bottom of the vat, leaving a boiling churning pulp above, and clearing the way to the bottom opening of the central agitating column. As soon as this is opened, and air has been admitted to the inner pipe, the spider is raised from the vat, and full agitation of the charge proceeds.

* *Min. and Sc. Press*, Oct. 1911.

The Brown vat has been adopted in South Africa at the Robinson, Crown, Brakpan, Modder B., and East Rand, and in Mexico and the United States, and at practically all new plants.

The Parral Vat.—Although the Parral vat has so far been employed in the treatment of silver-gold ores, containing chiefly the former metal, it will be convenient to consider it here, so that a comparison may be made with the Brown vat.

The Parral vat differs from the Brown vat in its height and diameter, being low and wide, and in the manner in which the agitation by air is carried out. A Parral vat, of what has been suggested as a standard size, is 25 feet in diameter, 15 feet in height, and holds about 90 to 100 metric tons of dry pulp.

A section of the Parral vat is shown in Fig. **132**. The bottom of the vat was formerly divided into two or more pockets or compartments, somewhat of the form of inverted cones or pyramids, by steel partitions, but these have been given up.

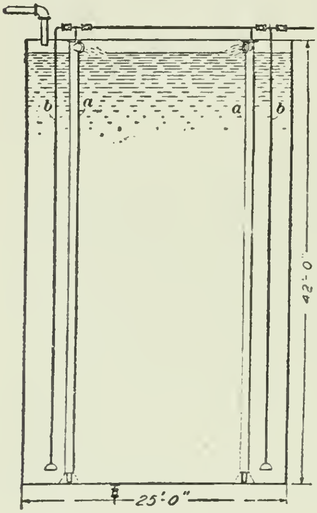

Fig. 132.—The Parral Vat.

Two or more transfer pipes, extending from the top to the bottom of the vat, are set near the sides of the tank. They are open at the bottom for the admission of the pulp, and for the admission of compressed air, by which the pulp is elevated. The upper ends of these pipes are fitted with L pipes, which are placed at such an angle that they deliver the pulp circumferentially to the side of the vat, and thus give it a whirling motion.

In working a charge, the pulp is fed in at the top of the vat. The necessary cyanide and lead acetate when required are placed on a grating below the inlet, and are dissolved during the introduction of the charge.

When the vat has been charged compressed air is forced in at the bottom of each of the transfer pipes; the pulp is carried up and delivered at the top of the charge. The agitation and circulation thus produced is continued until the treatment is completed.

One of the chief advantages claimed for the Parral vat, with its several air-lift pipes, is that if necessary it can be built of larger dimensions than a Brown vat with only a central air-lift.

Further, owing to its low height of 15 feet, the air pressure required is only 8 to 10 lbs. per square inch, as compared with from 30 to 40 lbs. for a Brown vat of 45 feet in height.

Trent Agitator.—The Trent agitator is a flat-bottomed vat (Fig. **133**).

Circulation is effected by means of a centrifugal pump, which draws the solution away from near the surface, and delivers it through a central axis into four arms arranged about 18 inches above the bottom. The arms are pipes, each carrying a row of nozzles inclined at an angle towards the bottom of the vat. A centrifugal pump, placed just outside the vat, draws the thin pulp from near the top of the charge, and forces it through the bottom of the vat into the arm pipes, which discharge it at the bottom of the charge.

The force of the discharge causes the agitator to revolve after the manner of a Butters and Mein's distributor. In order to aerate the charge and to aid in agitating it, air is fed in with the pulp going to the arms either by means of a separate air compressor, or by sucking air in with the pulp at the suction inlet of the circulation pump. The use of an agitator of this form has been advocated as a good means of bringing flat-bottomed vats up to an efficiency comparable to that obtained by Brown vats.

The Brown vats, however, require very little power, while the centrifugal pumps of the Trent vats may possibly require rather more. The power consumption cannot, however, be very great, as the pumps have to work against a very low head.

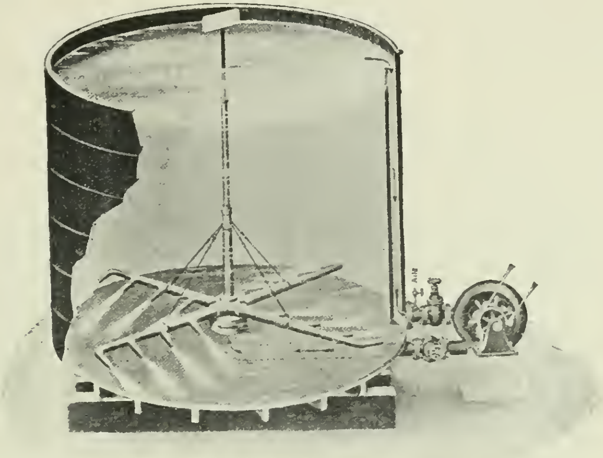

Fig. 133.—Trent Agitator (Fraser and Chalmers).

It is claimed that for 100 tons of dry slime 12 H.P. is required for this method.

The Trent agitators are in use at many cyanide plants, as, for example, at the Village Deep, S. Africa ; Porcupine, Canada, and all the important mines in Nevada.

The Hendryx Agitator (Fig. **134**).—This machine is intended for the treatment by cyanide of sand and slime, or of the pulp from the tube mills without classification. It consists of a cylindrical vat, with a conical bottom, fitted with a central tube up which the pulp is forced by the rapid revolution of screw blades.

It is claimed that this method of circulation is more effective than that obtained by the air-lift, or by centrifugal pumps, that by its use the gold is brought into solution within a few hours, and a short stoppage of the plant does not cause a hopeless clogging of solids at the bottom. The disadvantages are that more power per hour is consumed than by some other processes, but the less total time required must be taken into consideration when calculating the total power.

The report published by the Mines Trials Committee, S. Africa, gives details of the results of five tests on tailings from stamp mill amalgamation containing from 1⅔ to 2⅓ dwts. gold per ton. The average time of treatment was six hours, and the extraction varied from 85½ to 95 per cent. of the estimated gold content.

The pulp contained about 40 per cent. of plus 120-mesh and 60 per cent. of minus 120-mesh. In one test only slime was treated, and in two hours 92 per cent. of the estimated gold content was extracted.*

The Hendryx system gives good aëration, due to the use of the apron around the column pipe, whereby the pulp is being continually brought into contact with the atmosphere.

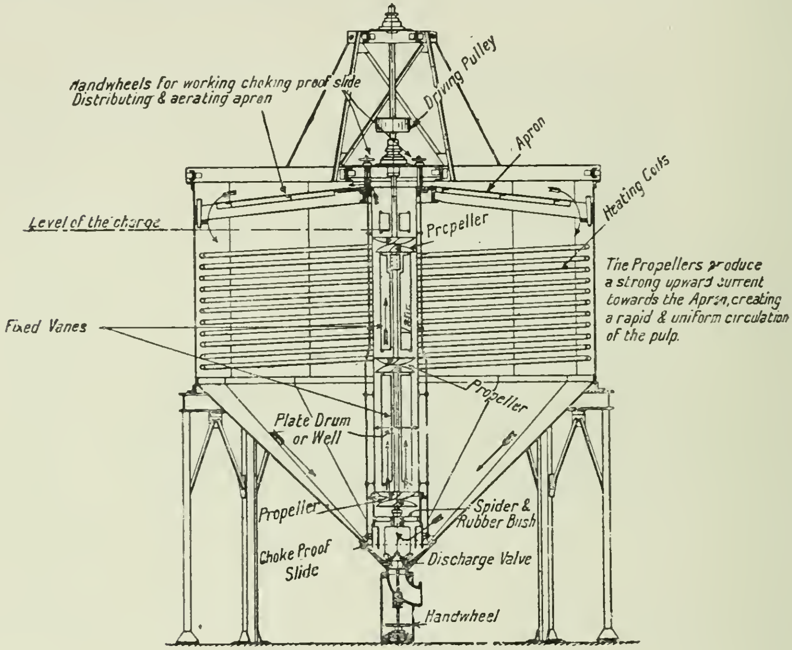
Handwheels for working choking proof slide
Distributing & aerating apron
Driving Pulley
Apron
Heating Coils
Level of the charge
Propeller
The Propellers produce a strong upward current towards the Apron, creating a rapid & uniform circulation of the pulp.
Fixed Vanes
Vane
Propeller
Plate Drum or Well
Propeller
Spider & Rubber Bush
Choke Proof Slide
Discharge Valve
Handwheel

Fig. 134.—Hendryx Agitator.†

The Dorr Agitator (Fig. 135).—The vat in which the mechanism works is flat-bottomed, and ranges in size from 16 feet diameter by 12 feet deep to 20 feet diameter by 12 feet deep; a much larger one, 40 feet diameter by 25 feet deep, has been recently erected.

The machine can be fitted to any flat-bottomed vat of suitable dimensions.

It consists of a central vertical cylinder, carried by a shaft supported from the top of the vat, and equipped with two arms, carrying ploughs, which revolve near the bottom of the vat and rake the pulp to the centre. The pulp is raised through the cylinder by means of air and discharged into revolving launders. The launders have openings at various points along their length, so that the pulp is evenly distributed over the surface of the charge. The circulation is thus down through the vat and up the air-lift cylinder in the middle. The air pipe for the supply of air for raising the pulp is fitted as shown in Fig. 135. The arms carrying the ploughs are hinged, so that, when it is necessary to shut down, they can be raised out of the settling pulp to stand up close to the cylinder.

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* *Min. Mag.*, vol. vii., Sept. 1912, p. 228.

† From block kindly supplied by the *Mining Mag.*

When the machine is started again they are gradually lowered to the normal position as the pulp becomes suspended. By this arrangement there is no danger of the arms being broken. The machine has the further advantage that the solids cannot accumulate and build up; the time and intensity of the agitation can be adjusted to meet the needs of the ore; the air-lift distance is low, and but little power is required for driving it. The arms revolve at slow speed, from 1 to 4 revolutions per minute, according to the nature of the ore. It is well adapted for continuous agitation, and has been installed at several important cyanide plants in America.

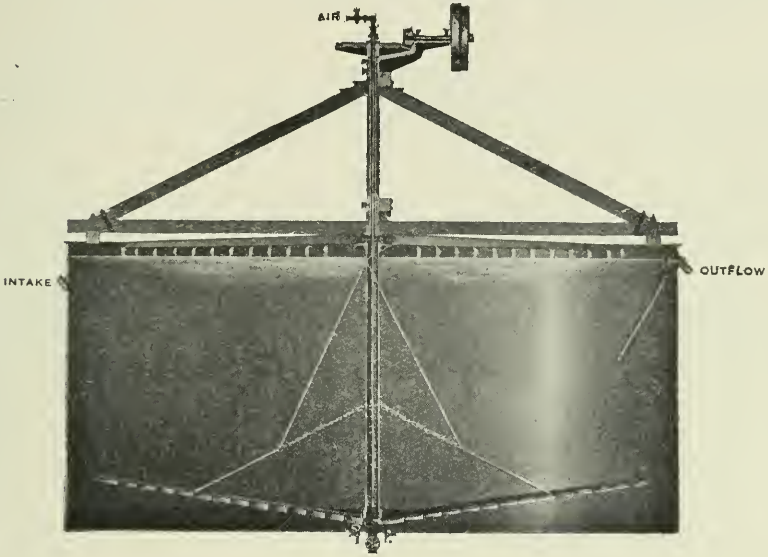

Fig. 135.—Dorr Agitator.

The Just Process of Agitation.—This process is carried out in a vat with a false bottom of porous silica bricks, below which air is forced in under pressure, and the air passing through the pores of the bricks keeps the pulp thoroughly agitated. The bricks are 2 inches in thickness, made of quartz sand, and are sufficiently porous to admit the passage of air without much pressure, but not so porous that the slime can pass through.

The vats are square, 20 feet by 20 feet and 10 feet deep, and are constructed of $\frac{1}{4}$-inch steel. They are divided into four compartments by steel partitions so arranged that the slime pulp may pass under and over them alternately.

The false bottom is formed of the porous bricks laid on 4-inch channel irons, and held down by light iron straps.

A vat of the foregoing dimensions has a capacity of 50 metric tons of dry slime when the ratio of solution to dry slime is 1·5 to 1.

The depth of the pulp is about 8 feet 6 inches. This depth was decided on in order that the air pressure required should not exceed about 5 lbs. per square inch, and thus would allow rotary blowers to be employed for supplying the air.

Both the Just agitator and the Trent agitator possess the advantage of being suitable for installation in existing vats with only slight modifications.

(5) **Slime Filtration.**—The mechanical appliances in use for filtration have been grouped as follows :—*

I. Suction filters, or filters in which a vacuum is used to accelerate filtration.

(*a*) Oliver and Ridgway filters. Appliances using a thin slime cake and practically continuous in their action.

(*b*) Moore and Butters' filters. Appliances using a thick slime cake and intermittent in their action.

II. Pressure filters, or filters in which hydrostatic head, compressed air, or pumps are used, in order to secure greater pressures than are possible with a vacuum pump.

(*c*) Ordinary filter presses.

(*d*) Sluicing filter presses (Merrill filter press).

(*e*) Filtering chambers or cylinders ; filters in which the filtering-basket is enclosed in a cylinder (Burt, Kelley, and Sweetland filter presses).

III. Centrifugal filters, or filters in which centrifugal force is used to separate solution from slime.

At present the suction filters are in greatest use. Of the pressure filters, the ordinary filter presses are going out of use, except as clarifying presses, and for pressing gold slime.

In the Merrill press, by the introduction of the sluicing system, the slime cakes can be washed out of the filter cells, and the press operated without opening or separating the filter plates for each charge. This improvement reduces the labour and cost, and increases the effectiveness of the filter press.

The Moore and Butters' filters both satisfactorily meet the requirements of slime filtration, with the exception that they are intermittent in their action, and to remedy this drawback the Ridgway and Oliver filters have been designed. Both filters are really very similar in construction.

In both suction is applied to the internal space between the canvas walls, by which solutions or wash water can be drawn through them and a layer or cake of slime left on their outer surfaces. But they differ in the method of operating them.

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* Young, *Min. and Sc. Press*, Oct. 1911.

The thickness of the pulp is important, but it must not be too thick to be handled with pipes and centrifugal pumps. A thick pulp is advantageous where much sand is to be held in suspension. In Nevada, with quartzose ores, pulp ratios of from 3 of solution to 1 of slime down to 1·5 of solution to 1 of slime are in use. The average pulp in use is 2 of solution to 1 of slime.

The Moore Filter is constructed of canvas, double, and sewn round three edges, the fourth (long edge) being bolted between strips of Oregon pine. Wire netting is also fitted between the canvas. In the bottom edge of each filter is a $\frac{3}{4}$-inch channel iron. The filters are stitched through both sides vertically at 4 inches apart, and in the compartments thus formed strips of wood 1 inch by $\frac{1}{4}$ inch are inserted to allow circulation.

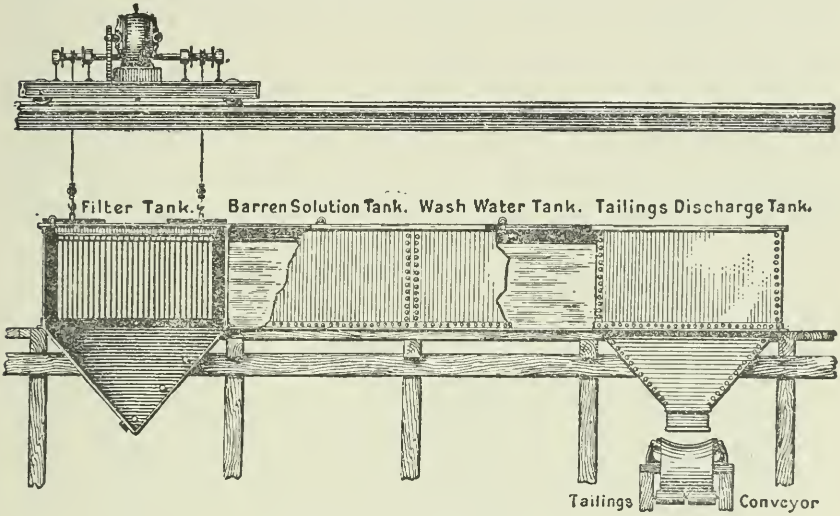

Fig. 136.—Moore Filter Vats.

Within each filter a 1-inch vertical suction pipe, flattened at one end to dip into the channel iron, reaches to the bottom. The upper end of this pipe is connected by suction hose with the main pipe through which the suction is applied. The dimensions of a filter leaf are 16 feet by 5 feet, and forty-nine are hung from a steel frame at distances of 4 inches apart, constituting a "basket." The basket is suspended from an overhead traveller, and can be raised, lowered, or traversed. The filtering process is carried on as follows:—The basket or frame of filters is lowered into the vat containing the slime pulp until submerged. Suction is applied by means of a suction pump, and continued until a cake of sufficient thickness, $\frac{3}{4}$ to 1 inch, or rather more, is obtained. The basket is then raised, the suction being kept on, and conveyed by the overhead traveller to the vat containing barren solution, into which it is lowered. After a sufficient amount of this solution has been drawn through the cake, the basket is again raised, and transferred to the wash-water vat. In this vat the cake is washed, suction being continued. After

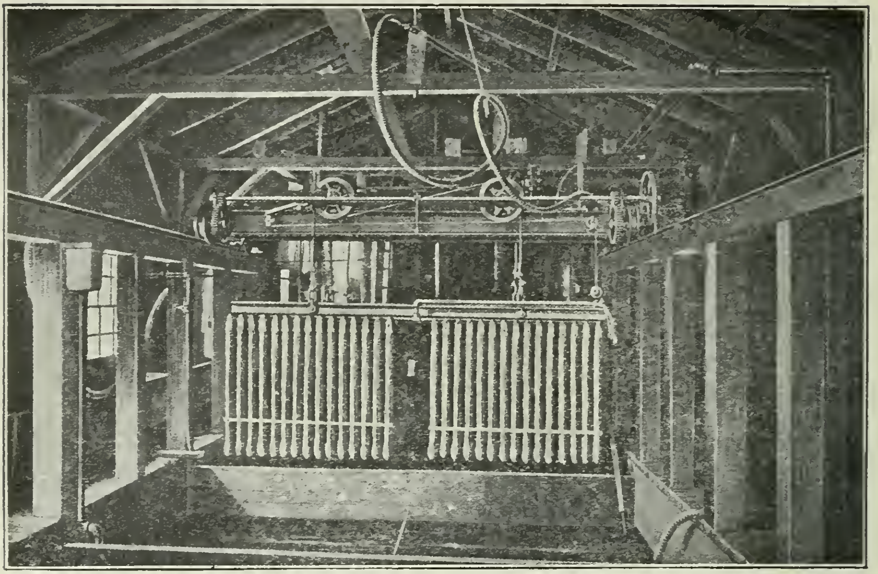

Fig. 137.—Moore Filter.

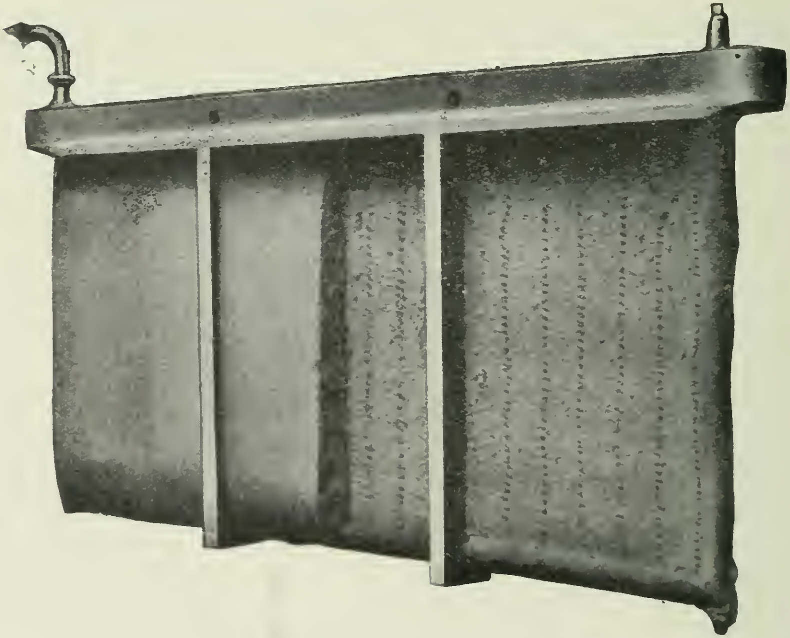

Fig. 138.—Butters' Filter Leaf.

this washing the basket is raised again and run over the discharge hopper, the suction being kept on until the excess of moisture has been removed. The cakes are then dislodged from the filter leaves by blasts of compressed air being forced inside them, and fall into trucks below. The arrangement of the vats is shown in Fig. 136.

The gold solutions pass to a clarifying tank, and then to the gold tank.

In Fig. 137 is shown a basket or group of frames with adherent slime about to be lowered into the barren solution vat.

The Butters' Filter.—Each filter leaf is made on a frame, the upper side being a bar of wood, 5½ inches wide, 1¾ inches thick, placed on edge, and 10 feet in length, or sufficiently long for its ends to rest on the top of the vat.

The other three sides are of ½-inch iron pipe, one end flattened and bolted to the wooden bar, and the other passing through the bar and connected with a vacuum pump. The upper face of the pipe forming the bottom of the frame is pierced with $\frac{5}{16}$-inch holes, 4 inches apart, and through these the solution passes from the filter.

The filter consists of a sheet of cocoa matting, to fill the inside of the frame, and on each side of this a sheet of 16-oz. canvas large enough to overlap the whole frame. These three thicknesses of material are sewn together by rows of stitching 1 inch apart. This filter is then fitted in the frame, the overlapping edges of the canvas being stitched round the outside of the piping. The upper edges of the canvas are fastened by being sunk in a groove, and a lath driven in over it. Each leaf is connected by short nipples and hose to the pipe leading to the vacuum pump. Five or six strips of wood are placed vertically on each side of the filter or leaf, and are screwed together to stiffen the frame and prevent the canvas from sagging.

The leaves or filter are placed in the vat at a distance of 4 inches from each other, centre to centre. A filter vat for 60 leaves is shown in Fig. 139. The filtering is conducted as follows :—The vat having been filled with sufficient slime pulp to submerge the filter, the vacuum pump, which draws the solution through the filter, is started, leaving the slime as a layer on the outside. The pulp is kept in agitation by air or other means. As the solution is withdrawn, fresh slime pulp is added to keep the level of the charge in the vat above the filter leaves. When the layer of slime has reached the proper thickness, about ¾ to 1 inch, the pulp in the vat is withdrawn. The vat is then filled with water, which is then drawn through the layer of slime to wash it. In some cases a weak cyanide solution is applied before the wash water. A filter leaf with cake of slime pulp attached is shown in Fig. 138.

When the washing is completed the vacuum is cut off and clear water introduced under slight pressure into the interior of the leaves. This dislodges the slime, and it and the water are then discharged through the discharge openings in the bottom of the vat.

A vat with 80 leaves treats 20 to 25 tons of slime per charge, the time required being about three hours.

The lime used in neutralizing acidity appears to protect the fibre.

When the calcium carbonate accumulates sufficiently to delay operations, it is removed by subjecting the leaves to a bath of 2 per cent. HCl. The filter box may be made either of wood or iron, as may seem advisable, depending on the locality, costs, and freight.

The Ridgway Filter (Figs. 140 and 141).—This machine consists of 14 cast-iron horizontal filtering frames, which rotate in a shallow circular tank about 13 feet in diameter, pretty much as the feed arms rotate around a buddle.

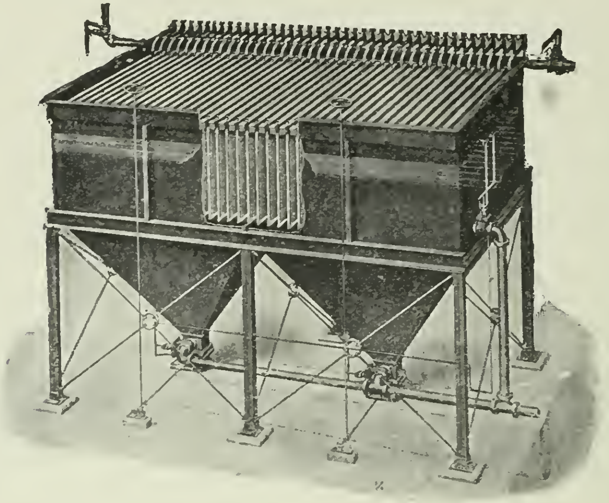

Fig. 139.—Butters' Filter Vat (Fraser and Chalmers).

The tank is divided into three compartments, into one of which the slime pulp is fed, the next having clear water, the third being open to permit of the frame contents being discharged into trucks or upon a conveyor. Each frame has an area of 4 square feet on its lower side, which is covered with filter cloth. These frames are arranged to be lowered into the pulp, raised over a partition, and lowered again into the wash-water compartment, and then raised over the next partition into the discharge compartment. The raising and lowering are effected by the arrangement of the rail on the edge

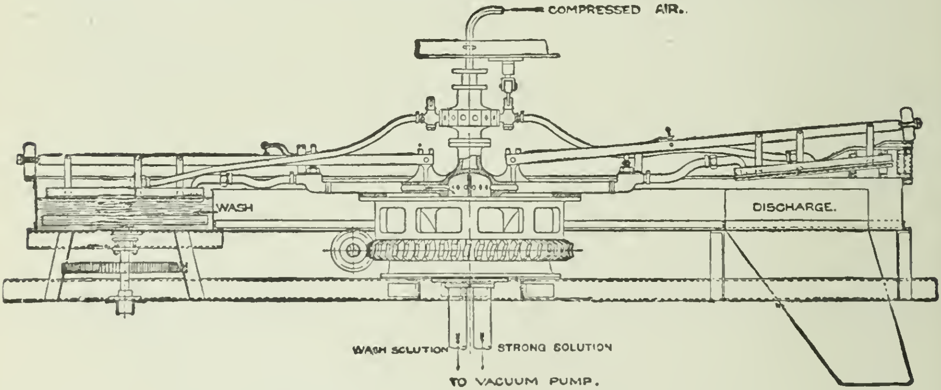

Fig. 140.—The Ogle-Ridgway Filter.

of the tank on which the rollers supporting each frame run. The vacuum valves for maintaining the suction, and the air-pressure valves for forcing off the cakes of slime, are operated automatically by cams ; in fact, the whole operation is automatic. As regards the thickness of the slime cake, the Ridgway filter utilizes a thickness of from 0·125 to 0·375 inch.

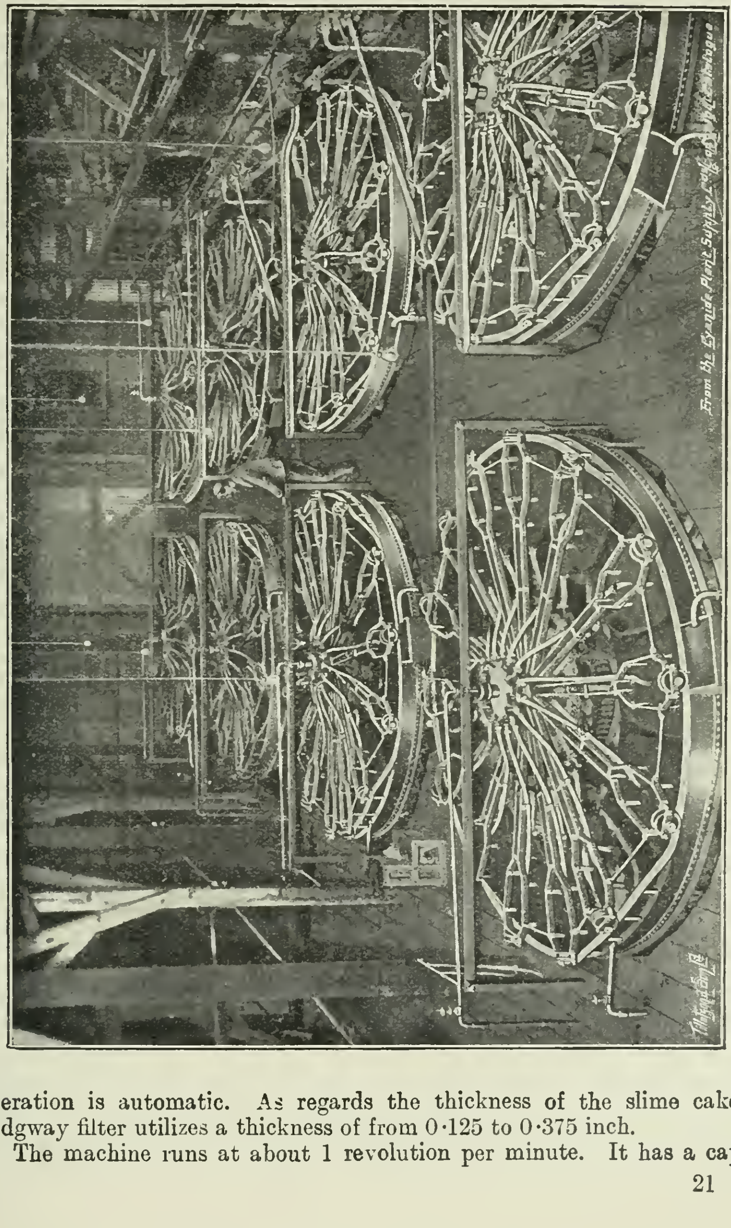
From the Cyanide Plant Supply Coy.'s Catalogue

Fig. 141.— Ogle-Ridgway Filter Plant.

The machine runs at about 1 revolution per minute. It has a capacity of about 30 to 60 tons per day, according to the character of the material treated.

The Oliver Filter (Fig. 142).—This filter consists of a drum, 11 feet 6 inches in diameter, and of lengths varying from 7 to 14 feet, revolving on trunnions, and immersed for three-fifths of the revolution in the slime pulp which is kept from settling by air agitation. The outer surface of the drum is divided by 1-inch strips into 24 sections. In these sections small strips are fitted to form channels for the passage of the solution.

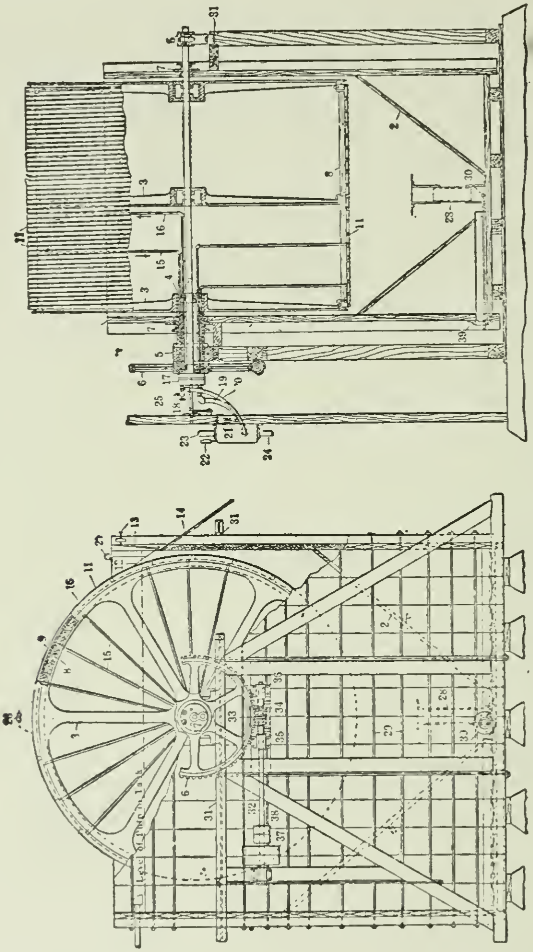

Fig. 142.—Oliver Filter (*Mining Magazine*, vol. ii., p. 313.)

Each section is provided with a vacuum pipe and a compressed air pipe, both of which pass through the hollow shaft supporting the drum. A wire screen is placed on the strips in each section. A layer of burlap and one of canvas is then laid on and firmly bound to the drum by winding steel wire round it.

In operating the filter, each section is connected with the vacuum apparatus while it is in the pulp, a cake of slime about $\frac{1}{4}$ to $\frac{1}{2}$ inch in thickness being accumulated on the canvas. On leaving the pulp the vacuum is still kept on to dry the cake. On reaching the top a water wash is given to the cake by a spray, and the water is drawn through it until the vacuum is cut off and the cake discharged. The discharge takes place just before the section re-enters the pulp, and is effected by cutting off the vacuum, introducing air under pressure, and by a scraper. The drum makes a complete revolution in four minutes, and one 8 feet wide will treat about 50 tons dry slime per 24 hours.

(6) **Filter Presses.**—It is held by some metallurgists that vacuum filters are best for clayey slime, and filter presses for slime containing much sand, but there can be no rule which is universally applicable, and a system of filtration which may be suitable for one ore may be impracticable for others.

There are two types of filter press, the Dehne and the Merrill.

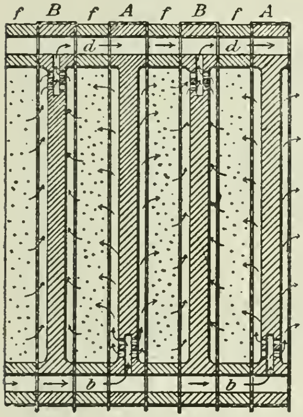

Fig. 143.—Dehne Filter Press (Section).*

The Dehne type of press is in extensive use in Australia, where the usual method is to agitate the slime in a vat with mechanical stirrers, to dissolve the gold, and then to pass the slime through a filter press, the press being used as a separating machine only.

This type of press has one disadvantage—viz., that the leaves have to be taken apart for the removal of the cakes of slime, the labour costs are hence rather high. They are, however, well suited for clarifying solutions before precipitation, and for the pressing of the gold slime from the zinc boxes. In the Merrill press the cakes of slime are removed by sluicing without opening the press.

The Dehne Filter Press.—This filter press consists of a number of cast-iron corrugated plates with a hollow frame between each two plates. Filter cloths are hung over the corrugated surface of each plate.

The plates and frames are arranged alternately in the press framing, each frame thus being a hollow chamber with sides of filtering cloth. The whole is firmly held together by screws, or bell-crank levers at one end of the framing. A press of standard size has 50 chambers, each 40 inches square, and will hold 9,000 lbs. of dry slime. The press is filled by forcing the pulp into the spaces between the filter cloths, when the liquor passes through the cloths and out through the outlet taps, while the slime forms a solid layer on the surface of each cloth until the whole space is filled with slime cake. The cakes formed range from 2 to 3 inches in thickness, according to the character of the material.

The solution containing gold is generally clarified by passing through another press before going to the precipitating boxes.

When the chambers are full the wash liquor is forced in at the bottom of every other plate, between the corrugations and the filter cloth, on one side only of each cake. It passes horizontally through each cake, and through the outlet at the top of every alternate plate, as shown in Fig. 143.

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* "Cyaniding Gold and Silver Ores," by Julian and Smart, p. 239.

When the washing is completed, compressed air is introduced to remove excessive moisture, the press is then opened, and the cakes discharged. The pulp and wash water are forced into the press by means of montejus, or pumps, a pressure up to 60 or 100 lbs. being required. The output per press is about 8 to 10 charges in 24 hours.

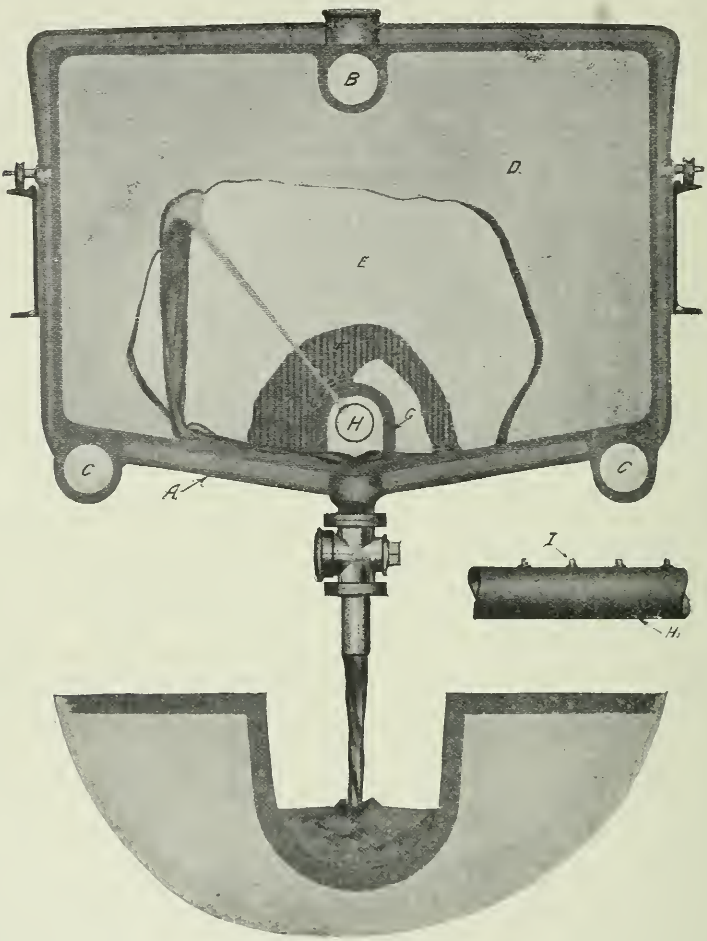

Fig. 144.—Merrill Press.

The Merrill Press (Fig. 144*).—The corrugated plates and hollow frames are placed alternately as in the Dehne press, but the inlets and outlets are arranged differently. The corrugated plates are covered with filter cloth as usual, and wash water, solutions, or air can be introduced between the cloths and the plates, on one side of the cell frames, containing the pulp through which they are forced by pressure. At the bottom of the press is a 2-inch or 3-inch pipe running its whole length and connected with the water supply. Projecting from this pipe into each frame compartment is a nozzle through which water, at about 60 lbs. pressure, is discharged against the cake of slime, while the whole pipe is turned backwards and forwards about its axis through an arc of about 200°. The slime is thus sluiced out through discharge pipes into a launder, by which it is carried away. The removal of the slime in this way without dismembering the press is an important advantage, saving both time and labour.

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* Rose, *Metallurgy of Gold*, p. 374.

The Merrill press can be used, not only as a filter, but also as a treatment press, and is employed for this purpose at the Homestake Mine in the following manner :—The slime, after being mixed with the necessary amount of milk of lime, is forced from a pressure tank into the press, which holds about 25 tons of slime. There are 28 presses in all. When the press is full of slime, air is drawn through for one hour for the purpose of aeration, after which weak cyanide solution is passed in for about half-an-hour, and then aeration is given for one hour. This is followed by strong solution and then weak solution each for an hour, and finally a water wash is given for one hour, when the spent slime is sluiced out.

The total time, including 70 minutes for filling, is about seven to eight hours, and the working strength of the solution 0·06 per cent. sodium cyanide. The Burt, Kelley, and Sweetland filter presses are only in limited use at present.

(7) **Clarifying Vats or " Clarifiers."**—These are vats of about 25 feet in diameter with a filter grating arranged as in sand leaching vats. This is covered with a jute mat and a cocoa-nut mat, upon which is laid about 12 to 18 inches of coarse sand. The slime which is deposited is shovelled off every two or three days.

The object of the clarifiers is to remove any slime which may be carried by the gold solutions from the treatment vats before they pass to the precipitation plant. In some plants this is effected by filter presses, but the tendency in S. Africa is to go back to filter vats.

Examples of the use of these various appliances will be found in the descriptions of the practice followed at typical works, pp. 339 to 351.

(8) **Precipitation.**—*The Siemens-Halske Electrolytic Process* for the precipitation of the gold has been abandoned, owing to its failure to effect complete precipitation, from 0·3 to 0·5 dwt. of gold being left in the solution, and the large amount of by-product produced by the decomposition of the iron anodes.

Aluminium and aluminium-mercury couple have been proposed and have been in use, but, while the precipitation of the gold is satisfactory, the insoluble alumina formed contaminates the precipitate and interferes with its conversion into bullion. It is, however, in successful use for the precipitation of silver.

Precipitation by zinc is the method in practically universal use.

A typical extractor box is shown in Fig. 145,* and a section of one of the compartments in Fig. 146. The extractor or zinc box on the Rand is generally

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* *Rand Met. Practice*, vol. ii., pp. 265 and 266.

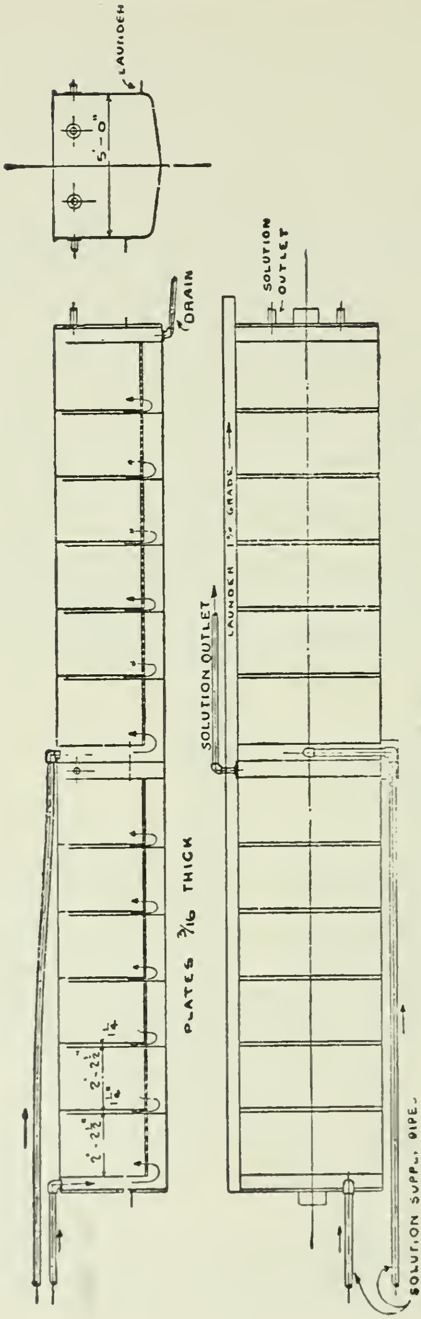
LAUNDER
5'-0"
DRAIN
SOLUTION OUTLET
SOLUTION OUTLET
LAUNDER 1% GRADE
PLATES 3/16 THICK
2'-2½"
1¼"
2'-2½"
1¼"
SOLUTION SUPPLY PIPE

Fig. 145.—Steel Extractor Box (ten compartments).

5 to 6 feet in width, and contains from 5 to 6 compartments, about 2 feet 2 inches to 2 feet 4 inches in breadth At some works the compartments are 7 to 10 in number. In new plants the boxes are constructed of steel, and not of wood.

The partitions between the compartments are arranged so that the cyanide solutions containing the gold pass upwards through the zinc, which is supported on trays of iron wire gauze or perforated sheet iron.

The last compartment is sometimes empty to act as a settler for any gold precipitate which may be carried over, or it may contain a sand filter.

In some plants the first and last have sand filters, all the others being filled with zinc.

In order to allow the solution to flow from compartment to compartment the extractor box has a fall of about $\frac{1}{4}$ inch per foot.

Each compartment is provided with an outlet pipe for running off the solution when the zinc is removed for dressing and at the clean-up, and another which is connected with the pump by which the precipitate is transferred to a filter press. At least two series of boxes are required, one being for the strong and one for the weak solution. The boxes and launders are fitted with locked covers. The solutions are allowed to flow slowly through the boxes, the rate of flow being determined by experience.

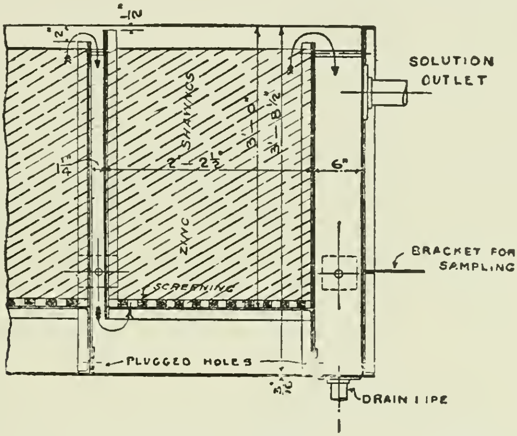

Fig. 146.—Extractor Box (detail of one compartment).

Generally the greater part of the bullion will be precipitated on the zinc in the first three compartments.

As the zinc in these first compartments settles down, zinc is transferred to them from the lower compartments, these then receiving fresh zinc.

The zinc is in the form of shavings freshly turned and of extreme fineness, about $\frac{1}{500}$ to $\frac{1}{1200}$ inch in thickness.

The turnings should be used, as soon as possible, after they have come from the lathe.

Before being placed in the boxes they are dipped in a solution of lead acetate, after which they should be covered with solution at once to prevent oxidation. The lead-zinc couple is more active than zinc alone; its use rapidly removes copper from solutions and prevents it from plating on the zinc shavings, which causes trouble in weak solutions.

"The principal conditions* on which satisfactory precipitation depends are :—(1) The freedom of the entering solution from solid matter in suspension ; (2) the presence of a sufficient amount of free cyanide ; (3) the presence of sufficient free alkali ; (4) the absence of excessive amounts of foreign salts, particularly of copper and iron compounds ; (5) a regular and uniform flow of liquid through the box ; (6) a sufficient volume of zinc per ton of solution to be precipitated per day ; (7) a clean, unoxidized surface, on which the gold and silver are deposited in a loose flocculent condition, easily detached.

If the gold becomes detached from contact with zinc it is redissolved if oxygen is still present, as precipitation is a process of reduction, or at least is favoured by reducing conditions and prevented by oxidizing conditions (Caldecott).

"When ordinary zinc shavings or filaments are used for precipitation, it is found that the precipitation of gold and silver is very much more effective in solutions carrying a fair amount of free cyanide than in solutions weak in cyanide. The strength of the entering solution should never be allowed to fall much below 0·2 per cent. KCN, and in some cases it is advantageous to allow a strong solution to drip slowly into the top compartment of the box, to ensure a sufficient strength for good precipitation. When the zinc-lead couple is used the matter is of less consequence, and very weak solutions can in general be precipitated by it."

A white precipitate occasionally coats the zinc in the upper compartments of the boxes and interferes seriously with the effective precipitation of the gold. It consists of zinc hydrate, zinc cyanide, and zinc-potassium ferro-cyanide. The exact cause of its formation has not been definitely decided, but absence of sufficient free alkali or of cyanide, and exposure of the zinc shavings to the air, appear to promote its deposition.

The arrangements of the zinc in the compartments requires special care in order that there may be no channels through which the solution may pass too freely, and the gold thus escape precipitation. The corners of the compartments need particular attention.

The boxes hence require "dressing," about every six or seven days, by re-arranging the zinc and replacing any that has been dissolved or is worn out

The precipitation of the gold is effected by the following reaction :—

$$2AuKCy_2 + Zn = ZnK_2Cy_4 + 2Au.$$

In practice, however, very much more zinc is required than is indicated by this equation, and from 6 to 16 ozs. are generally needed for each ounce of gold.

A consumption of 0·3 lb. of zinc per ton of ore is usual on the Rand, the chief amount being consumed in the treatment of the precipitate with acid.

Zinc Dust Precipitation by the Merrill Process.—This process was developed at the Homestake Mine, and is in use at several new plants in the United States, Canada, and Mexico, and at five or six plants on the Rand. It consists of a method of adding the zinc dust to, and mixing with, the gold-bearing solutions, and the use of a specially constructed filter press, into which the solution carrying precipitated gold with excess of the zinc dust is passed.

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* Clennell, *The Cyanide Handbook*, p. 248.

The essential features of the plant are shown in Fig. 147.

The precious metal-bearing solution is elevated from the sump tank to the filter press, the barren clear solution flowing from the press to the storage tank for re-use.

The zinc dust is spread upon the belt of the automatic feeder, which is arranged to deliver the zinc into the mixing cone in proper proportions to the volume of the solution pumped.

A small quantity of solution, together with compressed air, is charged by the pipes shown in the figure, into the mixing cone, where it becomes thoroughly mixed with the zinc dust, the mixture, or emulsion, as it is sometimes called, overflowing by a side pipe into the suction of the pump. The mixed stream of solution and precipitant is then pumped into the filter press, where the precious metals and excess of zinc dust are retained, the barren solution going to the storage tank.

The feed of zinc dust to the solution and of zinc dust and solution to the press requires careful supervision.

At the Dome Mill, Ontario, the zinc is added by a spiral screw conveyor, which feeds into a miniature tube mill, where the emulsion of the dust and solution is formed, the emulsion then passing into the stream of solution entering the press.

At the Homestake Mine, the admission of air to the mixer has been dis continued with advantage, and a continuous feeder used instead of the mixing cone, the consumption of zinc being decreased, and a more concentrated precipitate obtained. The zinc dust is carried from the feeder to a mixing cylinder, and thence to the pump section by a small stream of solution.

The advantages claimed for the use of zinc dust as compared with zinc shavings are :—

1. More efficient and rapid precipitation.
2. Lower consumption of zinc.
3. Less cost of zinc and labour.
4. A complete " clean-up " possible, whereas with zinc shavings a considerable proportion of the precious metals has to be carried over to the next " clean-up."

Further, " the difficulty of the *white precipitate* is avoided, and copper in the solution is not prejudicial when zinc dust is used. By the Merrill system, too, the zinc is always kept from the air and wet and surface oxidation is thereby prevented. On the other hand, the short time of contact and the incompleteness of the zinc-lead couple formed in zinc-dust precipitation are against its adoption in dealing with very dilute or poor gold solutions." *

It has not yet been shown whether zinc in the form of dust is more advantageous than shavings for precipitation generally. The precipitation is about equally efficient, but with the exercise of great care and skill better results and a higher grade precipitate can be obtained with dust than with shavings.

According to Alfred James, however, the recent trials of the zinc-dust

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* Rose, *op. cit.*, p. 384.

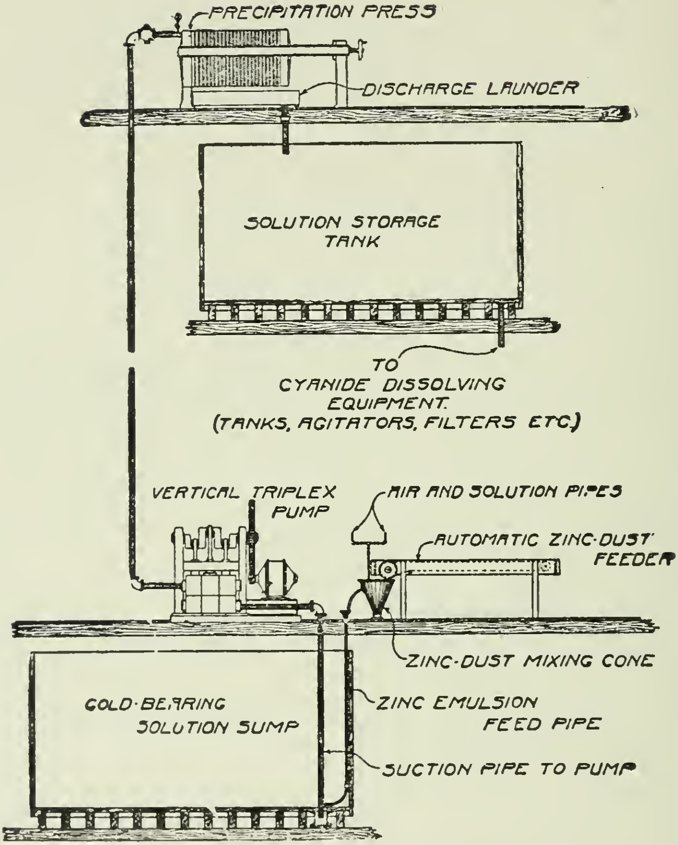
PRECIPITATION PRESS
DISCHARGE LAUNDER
SOLUTION STORAGE TANK
TO CYANIDE DISSOLVING EQUIPMENT. (TANKS, AGITATORS, FILTERS ETC.)
VERTICAL TRIPLEX PUMP
AIR AND SOLUTION PIPES
AUTOMATIC ZINC-DUST FEEDER
ZINC-DUST MIXING CONE
GOLD-BEARING SOLUTION SUMP
ZINC EMULSION FEED PIPE
SUCTION PIPE TO PUMP

Fig. 147.—Arrangement of Merrill Precipitation Plant.

method in South Africa confirm the superiority of the zinc box shaving method for its special work in that district.

The Clean-up.—The clean-up takes place either once or twice a month, sometimes, but rarely, weekly.

The flow of the gold-bearing solution into the zinc box to be cleaned up is stopped, and the clear solution in the compartments is carefully drawn off down to the level of the grating supporting the zinc, the solution being transferred to the first compartment of another box.

Clean water is run through the boxes, in order to thoroughly wash out all soluble cyanides. In small works the zinc shavings in the first compartment are then carefully rubbed between the fingers, to dislodge adherent precipitate. The tray is removed, and the shavings further washed over the next compartment. The clear liquor is siphoned off, and the precipitate run out by the launder in front of the boxes through a 40-mesh sieve into a receiving vat, where it is allowed to settle, the settlement being sometimes promoted by the addition of alum.

The gold precipitate passes through the sieve, and the small zinc remaining behind is rubbed to further separate any precipitate adhering to it. When the precipitate has settled it is washed two or three times by decantation, the liquor being run into a settling vat to collect any precipitate which may be carried over. After washing it is collected and treated by one of the methods mentioned below.

In large works the washing of the zinc is very efficiently performed by using a trommel devised by J. E. Thomas.

The trommel is a cylinder, with a suitable screening, carried on bearings constructed to fit the sides of a compartment and allow the trommel to be moved from one compartment to another. The method of using it is described by Thomas as follows :—*

"After the trommel is in position over the compartment, in which the zinc shavings are to be washed, the latter is filled with water or solution, so that from one-third to one-quarter the diameter of the former is submerged. The door is then opened and enough shavings put in to barely half-fill the trommel, and the door closed. The trommel is then rotated on its axis by means of handles till the shavings are sufficiently washed. The door is then opened ; the shavings inside are taken out and put back into the precipitation boxes. More shavings are put into the trommel, and so on, till all the shavings to be washed have been done. The turbid liquid in the compartment and the precipitate are then pumped through a filter press, and the fine zinc remaining taken to the acid vats, or dried for fluxing."

The shavings and coarse fines are now put back into the compartment, and the other compartments are similarly successively treated. The old zinc from these is transferred to the upper compartments until they are full, the lower compartments only being charged with fresh zinc.

The precipitate in the press is washed with hot water, and, finally, partially dried by compressed air.

The Crowe Process.—As has already been pointed out (p. 328), precipitation is a process of reduction, or at least is favoured by reducing conditions and prevented by oxidizing conditions. Hence the less air contained in the solution, the better it will be for the success of the operation.

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* *J. C. M. and M. Soc., South Africa*,, vol. iv., p. 315.

By the Crowe process a continuous vacuum is applied to the pregnant cyanide solution during its flow to the precipitation presses, whereby the dissolved air is removed from the liquid (see p. 348).

According to Crowe, the air dissolved in the solution has, owing to the different coefficients of absorption, a composition of 35 per cent. of oxygen and 65 per cent. of nitrogen, and consequently is a more active oxidizing agent than air of normal composition. He points out that in weak cyanide solutions, consequently with a minimum of hydrogen being generated, the oxidizing action of the dissolved oxygen largely neutralizes the reducing action and may even overcome it. In normal practice this is met by adding lump cyanide at the head of the precipitation box, with consequent increased consumption of both cyanide and zinc. By the adoption of the vacuum process, this practice is unnecessary, and extraction may be effected with weaker solutions resulting in savings in all departments, including the production of a purer bullion. The Portland Gold Mining Company reports a saving of $30,000 per year in zinc and cyanide in a plant treating 2,000 tons of ore per day (Picard).*

Precipitation by Charcoal.†—At the Yuanmi Mine, Western Australia where an auriferous deposit containing arsenic and antimony is worked, finely ground charcoal has displaced zinc in the precipitation of gold from the cyanide solutions, giving a better recovery than when zinc dust precipitation was used, higher-grade bullion, and at a smaller cost. Fine grinding of the charcoal is essential; it must be carried beyond anything measurable by screen tests, but there would appear to be a point beyond which it is inadvisable to proceed. In practice this point is arrived at by the time allowed for grinding. The grinding is effected in a small ball mill, 6 feet by 1 foot 11 inches inside diameter, containing steel balls. Charcoal quenched in water when red hot and then wet-ground is superior to the air-cooled dry-crushed product.

The process is carried on as follows:—Precipitation is effected by filtration in extractors designed by Moore and Edmands, drawings of which are given in Fig. 147*a*. The filter frames are 2 feet 3 inches by 2 feet 9 inches, and are spaced 4½-inch centres. The filter media are respectively cocoa-nut matting as a support, filter cloth or duck, and an outer cover of calico. Each frame is connected to a manifold, which, in its turn, is connected to a vacuum pump. Agitation is provided for by four propellers on a horizontal shaft.

The operation is conducted preferably in three stages.

The gold-bearing cyanide solution is run into an extractor and charcoal pulp (say 300 lbs. dry weight charcoal) is pumped in. The propellers are then started and allowed to run during the whole operation. A vacuum is started as soon as the filter leaves are properly submerged, a cake being quickly formed on each leaf.

Fresh solution is fed in continually for 24 hours, when the vacuum is released, the charcoal re-emulsified, and the cakes reformed by restoring the vacuum. The 300 lbs. of charcoal remains in each of the three extractors for nine days. The extractors are worked in series. The extractor containing the charcoal cakes nearly saturated with gold receives the gold-bearing solu-

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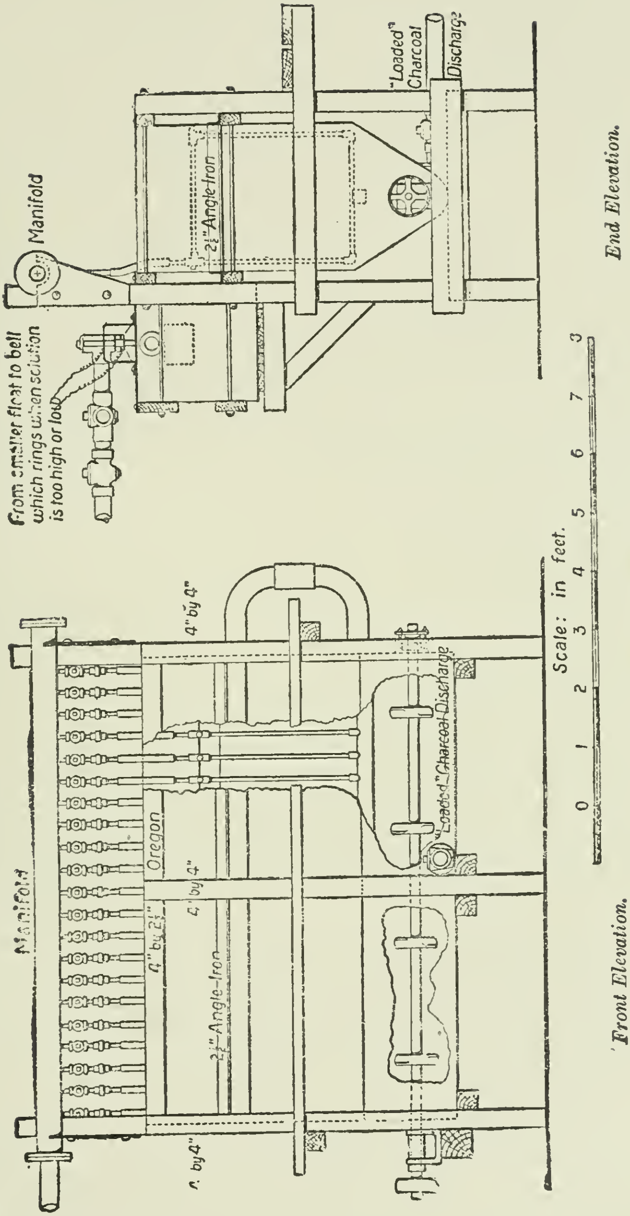
* H. K. Picard, Presidential Address, *Trans. Inst. Min. and Met.*, 1919, vol. xxviii., p. 34.

† H. R. Edmands, *Trans. Inst. Min. and Met.*, vol. xxvii., p. 277.


Manifold
Manifold
From smaller float to bell
which rings when solution
is too high or low
"Loaded"
Charcoal
Discharge
2½" Angle Iron
4" by 4"
4" by 4"
4" by 2½"
4" by 4"
Oregon
2½" Angle-Iron
"Loaded" Charcoal Discharge
Scale: in feet.
0
1
2
3
4
5
6
7
8

Front Elevation.

End Elevation.

Fig. 147*a*.—Moore-Edmands Extractor.

tion first, the tails from which are passed to the next extractor, and the tails from this are led to the other extractor, which is charged with fresh charcoal.

When sufficiently charged with gold the vacuum is released, the charcoal emulsified, and the pulp delivered to a clean-up press, washed, and dried with compressed air. The cakes are then ready for burning without any further drying. The burning of the charcoal is carried out in braziers, 18 inches by 18 inches by 18 inches, made of stout wire screening ½-inch or ⅜-inch aperture. A few hot coals are placed in the bottom, and the cake from the press is shovelled in. In about 48 hours the whole of the carbon is consumed. The burning is carried out in a locked chamber of sheet steel accommodating 16 braziers. The ash at present is melted with fluxes in a tilt furnace using graphite pots. The ash contains from 10 per cent. to 14 per cent. fine gold, and the bullion averages Au 954·4, Ag 7 parts per thousand.

The amount of solution treated per day ranges from 350 to 420 tons.

Treatment of the Gold Precipitate.—The gold precipitated by zinc will contain more or less zinc fines, some lead derived from the dissolved zinc, and also copper, if this metal was present in the cyanide solution. Several methods are in use for the production of marketable bullion from the precipitate, their object being the elimination of zinc and other impurities as far as is economically practicable.

The most important are :—

1. Direct fusion with fluxes.
2. Fusion after roasting.
3. Treatment with sulphuric acid or hydrochloric acid, with subsequent fusion.
4. Tavener process.
5. Rose's process, see p. 356.
6. Fusion after volatilization of the zinc.

In all cases great care must be taken to avoid loss by "dusting."

1. **Direct Fusion.**—The precipitate, after being dried in iron pans, is mixed with borax, sodium carbonate, nitre, and sand, in various proportions, according to the amount of zinc present. Nitre should be avoided whenever possible, but must be used if the precipitate contains much zinc. The bullion may be very impure, containing Zn, Pb, and Cu, and the method is hence not often employed.

2. **Fusion after Roasting.**—The precipitate, sometimes mixed with nitre, is placed in iron trays in a muffle furnace, and when dry the temperature is raised to a dull red heat to oxidize the zinc. The roasted product is then mixed with fluxes, as in the previous method, and melted in crucibles. In some of the large plants, where this method was employed, the melting with fluxes was carried out in Faber du Faur tilting furnaces (see Fig. 86, p. 236).

3. **Acid Treatment.**—This is in more extensive use than the other methods. The zinc-box precipitate, after collection in the receiving vat, or as is sometimes the case in the acid vat, or after having been transferred to the latter, is treated with sulphuric acid to dissolve out as much as possible of the zinc it contains. The acid vats may be of wood, or wood lined with lead, and should be fitted with a two or four-armed stirrer having reversible gear,

Their dimensions are usually 6 to 10 feet in diameter and 5 to 6 feet in depth. They should be provided with hoods and closely-fitting covers with two openings, one for charging which can be closed by a door, and the other for the escape of fumes. To the latter is fitted a wide tube of wood or iron, which passes up through the hood, so that the fumes which contain arseniuretted hydrogen and are poisonous may be delivered into the open air. In some works there is a vertical row of plugged holes in the sides of the vats for drawing off the liquor and wash waters. Water is charged in, if necessary. and sulphuric acid added in successive quantities, care being taken to avoid frothing over.

Exhaust steam is passed in at some mills and the stirrer revolved from time to time. When all action has ceased, the vat is filled with water, and the precipitate allowed to settle. On the Rand, where the precipitate has been filter-pressed, dilute sulphuric acid containing about 10 to 12 per cent. of acid is first charged into the vats. The zinc-gold slime is then added very carefully, to avoid excessive ebullition and " boiling over " of the charge, and is continued until all action ceases, or until the absence of free acid is shown by methyl-orange.

The supernatant liquor is run off through the plug holes into a settler, and the precipitate, after being washed with hot water two or three times to free it from acid and zinc sulphate, is drawn off through an outlet at the bottom of the vat. It is better, however, and this is the practice in large works, to pump the whole through a filter press in which the precipitate is washed with water and dried by compressed air.

In either case, the precipitate is dried in sheet-iron trays in a muffle, and heated to redness.

The dried and calcined material is melted in plumbago crucibles with clay liners, with fluxes, which, on the Rand, are usually manganese dioxide, ground fused borax, and sand, to which fluorspar is sometimes added.

The function of the first is to oxidize the base metals present in the slime, and prevent them from passing into the bullion ; it tends, however, to carry silver into the slag, so that as little as possible should be used, although the silver is recovered by the Tavener process, which is frequently employed in connection with fluxing for the treatment of slags, slime, etc. The borax gives fluidity, and the sand prevents the liner from being corroded.

At some plants the precipitate is fused with sodium carbonate 10 to 20 per cent., borax 20 to 60 per cent., and with or without sand, according to its composition.

The ingots obtained are generally remelted and cast into bars of bullion, which will range in fineness between 850 and 985 gold and silver. The fusion with fluxes is frequently performed in Faber du Faur tilting furnaces (see Figs. 86-89, p. 236), fired either with coke, oil, or gas. Where these furnaces are used, the bullion is usually remelted in crucibles in ordinary air furnaces.

In carrying out the acid treatment, sodium bisulphate has been introduced during recent years instead of sulphuric acid, on account of its cheapness ; a larger plant and an extra vat for dissolving the bisulphate, however, are required.

4. **The Tavener Process.**—Lead smelting of the zinc-box precipitate. In this process the zinc-box precipitate is smelted in a small reverberatory furnace with litharge, fluxes, and reducing agents, producing auriferous lead,

which is afterwards cupelled to obtain the gold. The clean-up of the zinc boxes is made in the usual way, except that the whole of the precipitate from the clean-up tub is pumped into a filter press.

The following description is abstracted from an account of an actual smelting by L. A. E. Swinney.* The cakes of precipitate from the press were dried in cast-iron trays, passed through a coarse sieve, and melted with fluxes and reducing agents in the following proportions :—PbO 120, C 10, assay slag 55, Fe 13, SiO_2 25 parts. The C was in the form of small coal, the Fe as tin plate scrap, or old tins cut into small pieces, and the SiO_2 as clean sand from the tailings.

Only 5 per cent. of the iron was mixed with the charge, the remaining 8 per cent. being added near the end of the process. The charge was thrown into the furnace, where previously some lead bullion from the smelting of by-products had been placed, and was covered with some of the litharge. The fire was then lighted and the charge slowly melted, with occasional rabbling.

When all action had ceased, the slag was skimmed off, the taphole opened, and the lead run into moulds. The lead should not contain more than 8 per cent. of gold.

The lead bullion obtained by this method of smelting is cupelled in an English cupellation furnace until a cake of gold alone remains on the cupel or "test." This is allowed to cool, and during solidification is carefully broken into pieces.

The pieces are melted in crucibles and cast into bars, which should be of a fineness of from 960 to 980 gold and silver in 1,000 parts.

The cost of the process is said to be less than that of the acid treatment, and in experiments made, on a large scale, by the Fereira Gold Mining Company the loss of gold was very small.

The slags from the reverberatory furnace are smelted in a small blast furnace with other by-products, such as assay slags, old cupellation "tests," old crucibles, extractor-house sweepings, etc., and the lead bullion produced is cupelled with that from the reverberatory furnace.

The Chemical Reactions and Changes which occur in the Cyanide Process. —The chief chemical reactions on which the cyanide process as ordinarily conducted depends are the following :—

Solution of the Gold.

$$(1)\ 4Au + 8KCy + O_2 + 2H_2O = 4KAuCy_2 + 4KHO$$

in which the gold is dissolved by potassium cyanide.

According to Bodländer, the action of the cyanide takes place in two phases, as follows :—

$$(a)\ 2Au + 4KCy + 2H_2O + O_2 = 2KAuCy_2 + H_2O_2 + 2KHO.$$
$$(b)\ 2Au + 4KCy + H_2O_2 = 2KAuCy_2 + 2KHO.$$

And

Precipitation of the Gold by Zinc.

$$(2)\ 2KAuCy_2 + Zn = 2Au + K_2ZnCy_4.$$

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* *Trans. Inst. Min. and Met.*, vol. xvi., pp. 115 125.

According to Christy the reaction is—

$$2KAuCy_2 + 3Zn + 4KCy + 2H_2O = 2Au + 2ZnK_2Cy_2 + K_2ZnO_2 + 2H_2.$$

According to Clennell—

$$KAuCy_2 + 2KCy + Zn + H_2O = Au + K_2ZnCy_4 + KHO + H.$$

The precipitation is only active in the presence of excess of KCy.

As regards the solution of the gold, J. S. Maclaurin has demonstrated "that the rate of dissolution of pure gold, in the form of plates, in potassium cyanide solutions passes through a maximum when proceeding from dilute to concentrated solutions. The maximum is reached when the solution contains 0·25 per cent. of KCy.

"The solubility of gold is very slight in solutions containing less than 0·005 per cent., but increases rapidly as the strength rises to 0·01 per cent., when the rate of dissolution is ten times as great as in the 0·005 per cent. solution, and about half as great as that in the 0·25 per cent. The rate increases slowly as the strength rises to 0·25 per cent., and thereafter decreases much more slowly, until in 15 per cent. solutions the rate of dissolution is about equal to that in 0·01 per cent. solutions.

"Higher strengths show a gradual diminution in the rate of dissolution up to saturation point.

"Silver is also dissolved at a maximum rate in solutions containing 0·25 per cent. of cyanide, and the changes in the rate are similar to those noted above in the case of gold, the rates for silver being always about two-thirds of the corresponding rates for gold, or roughly, in the same ratio as the atomic weights of the two metals.

"In both cases there is not very much change in the rate of solubility as the strength rises from 0·1 per cent. to 0·25 per cent."*

From equation (1) it is seen that free oxygen is required for the solution of the gold, and hence aeration of the charges in the leaching vats is practised.

In order to effect the same result, the addition of various oxidizing reagents to the cyanide solutions have been proposed, such as potassium permanganate, potassium chlorate, alkaline peroxides, hydrogen peroxide, potassium ferricyanide, etc., but so far none of them has come into use in actual practice.

When cyanogen bromide, however, is added to cyanide solutions, the presence of oxygen is not required, and their power of dissolving gold is markedly increased.

$$3KCy + 2Au + CyBr = 2KAuCy_2 + KBr.$$

Cyanogen bromide is in use in W. Australia and the Cripple Creek district. Colorado, in the treatment of telluride ores (see pp. 349 to 351).

Decomposition of Potassium Cyanide Solutions.—Potassium cyanide in the presence of air is oxidized, potassium cyanate being formed, thus—

$$2KCy + O_2 = 2KCyO.$$

The cyanate also decomposes, potassium carbonate and ammonia resulting—

$$2KCyO + 3H_2O = K_2CO_3 + CO_2 + 2NH_3.$$

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* *Journ. Chem. Soc.*, vol. lxiii., p. 731, quoted in Rose's "Gold," p. 352.

Potassium cyanide is also decomposed by carbon dioxide when moist or in solution, hydrocyanic acid being set free and potassium carbonate formed—

$$2KCy + CO_2 + H_2O = 2HCy + K_2CO_3.$$

In ordinary cyanide solutions, however, these changes take place very slowly, so that the injection of air into the solutions or charges of the ores in the vats may be practised with impunity, and the action of CO_2 is prevented by the presence of a slight excess of alkali.

Serious decomposition of KCy, however, results from the presence of the so-called "cyanicides" in the ores, and this may lead to excessive consumption of the salt. The most important of these will now be considered.

Iron Pyrites.—Pure cubical iron pyrites has almost no action, if any, on potassium cyanide solutions; on the other hand, marcasite, the rhombic form of iron pyrites, is specially prejudicial, as it so readily undergoes oxidation. When tailings have been exposed to the weather the iron pyrites is oxidized by the action of air and water to ferrous sulphate and free sulphuric acid.

$$FeS_2 + H_2O + 7O = FeSO_4 + H_2SO_4.$$

The ferrous sulphate becomes still further oxidized to ferric sulphate, $Fe_2(SO_4)_3$, a basic sulphate and ferric oxide are also formed.

The ferric oxide has no action on KCy, but the other compounds are most destructive, thus—

$$H_2SO_4 + 2KCy = K_2SO_4 + 2HCy.$$
$$FeSO_4 + 2KCy = FeCy_2 + K_2SO_4.$$

The $FeCy_2$ acts in its turn on the KCy, giving rise to potassium ferrocyanide.

$$FeCy_2 + 4KCy = K_4FeCy_6.$$

The potassium ferrocyanide in the presence of $FeSO_4$ forming a precipitate, $K_2Fe_2Cy_6$.

$$FeSO_4 + K_4FeCy_6 = K_2Fe_2Cy_6 + K_2SO_4$$

This precipitate is oxidized in presence of air and free acid to Prussian blue, $3FeCy_2 2Fe_2Cy_6$.

$$4K_2Fe_2Cy_6 + O_2 + 2H_2SO_4 = 3FeCy_2 2Fe_2Cy_6 + K_4FeCy_6 + 2K_2SO_4 + 2H_2O.$$

In the presence of free alkali the formation of both these is reduced to a minimum.

"It follows from these reactions that if the blue colour of Prussian blue is visible in the vats or on the surface of the tailing heaps an enormous waste of cyanide must have taken place" (*Rose*).

Ferric sulphates also cause a loss of cyanide.

$$Fe_2(SO_4)_3 + 6KCy = Fe_2Cy_6 + 3K_2SO_4.$$
$$Fe_2Cy_6 + 6H_2O = Fe_2(OH)_6 + 6HCy.$$

Ferrous hydrate when formed by the presence of alkali consumes cyanide, thus—

$$Fe(OH)_2 + 6KCy = K_4FeCy_6 + 2KHO.$$

Ferric hydrate has no action on KCy.

Copper pyrites dissolves but slowly until oxidized. Copper sulphate, when present from the oxidation of copper pyrites, gives rise to the formation of a double cyanide of copper and potassium.

$$CuSO_4 + 4KCy = CuK_2Cy_4 + K_2SO_4.$$

Copper carbonate, whether artificial or native, is one of the most troublesome cyanicides. According to Clennell, the reaction which occurs is as follows :—

$$2CuCO_3 + 7KCy + 2KHO = Cu_2Cy_2(KCy)_4 + KCyO + 2K_2CO_3 + H_2O.$$

Zinc blende has but little action on cyanide solutions, but the hydrate and carbonate cause loss of cyanide, zinc cyanides being formed.

$$ZnCO_3 + 2KCy \quad = ZnCy_2 + K_2CO_3$$
$$Zn(HO)_2 + 2KCy = ZnCy_2 + 2KHO$$

Loss of cyanide may arise from the presence of amalgam in the tailing when amalgamation has been practised ; also from manganese oxides in the ores.

As regards the precipitation of the gold, the equation (No. 2) already given represents the reaction which takes place in the zinc-boxes where the gold in the solutions is precipitated by zinc.

By this reaction the KCy solutions are decomposed and become weaker, and a certain amount of zinc is dissolved. A large amount of zinc, however, is dissolved by the KCy in the solutions, and as the result of the following reactions, so that very much more is required in practice than in theory.

For example, the contact between the zinc and the gold and between the zinc and the lead it contains determines an electric current, which decomposes water, the oxygen of which attacks the zinc.

$$Zn + 2H_2O = ZnH_2O_2 + H_2$$

The zinc hydrate formed dissolves in the KCy

$$ZnH_2O_2 + 4KCy = K_2ZnCy_4 + 2KHO.$$

Further, this KHO attacks the zinc, forming zincate, which dissolves in the KCy, a double cyanide of zinc and potassium resulting.

$$Zn + 2KHO = K_2ZnO_2 + H_2.$$
$$K_2ZnO_2 + 4KCy + 2H_2O = K_2ZnCy_4 + 4KHO.$$

Zinc potassium cyanide in the proportions usual in ordinary working cyanide solutions has no injurious effect on their solvent power for gold. Feldtmann, Goyder, and others have shown in fact, that K_2ZnCy_4 has a solvent action on gold in ores.

" At the Mercur Mine the stock solution was apparently as efficacious after nine months' use as at the start. although it must have contained large quantities of zinc cyanide " (*Rose*)

EXAMPLES OF CYANIDE PRACTICE.

The following details of one of the later mills erected on the Rand are taken from the " James Forrest " lecture by Dr. Hatch, delivered at the Institute of Civil Engineers, 28th June, 1911 :—

The City Deep Mill.—" This mill is designed to handle 65,000 tons of ore per month, and is equipped with two hundred 2,000-lb. stamps and nine 25- by 5½-foot tube mills, each unit of ten stamps being operated by a 50-H.P. motor, and each tube mill by a 100-H.P. motor. The ore from the mine is divided into two classes by screening through grizzlies ; the fine material is conveyed by a 20-inch belt direct to the main ore-bin ; the coarse is taken by four inclined sorting-belts to the crushers, each belt feeding three 12- by 24-inch jaw crushers. The return portion of each sorting-belt receives the rejected 'waste,' and delivers it to a belt, which conveys it to the waste-dump. In the stamp battery the ore is crushed to pass a 10-mesh discharge screen. The resulting pulp, after elevation by a sand pump, is classified in cones, and the coarse product is delivered to the tube mills. The product from the tube mills, together with the overflow from the classifying cones, is conducted to amalgamating tables in the gold-recovery house. In this house are also placed the extractor boxes for the enriched cyanide solution, the clean-up machinery, and the refinery, so that all the operations connected with the recovery of the gold are performed in one building under the immediate supervision of the ore-reduction officer. The pulp from the amalgamating tables is again elevated by a Robeson pump and classified, the sands being collected in six conical-bottomed collecting vats of re-inforced concrete, 50 feet in diameter by 10 feet deep. A 24-inch conveyor belt, running under the centre line of these vats, takes the sand, excavated from them by a Blaisdell excavator, elevates it and delivers it by means of a belt, running at right angles to the top of the sand-leaching plant, which comprises two rows of six vats each. The sand is fed in by a Blaisdell distributor, and, after leaching, is discharged by a Blaisdell excavator through central shoots to two 24-inch conveyor belts, one under each row of vats. A short cross belt delivers it to a 24-inch inclined belt, which conveys it to the residue-dump. The slime is collected in four conical-bottomed collectors built of re-inforced concrete. It is treated in two steel conical-bottomed air-agitation vats, 32 feet in diameter by 38 feet deep, and washed in eight steel conical-bottomed wash vats, 70 feet in diameter by 16½ and 23½ feet deep."

In the plant just described it will be observed that from the moment the ore is delivered at the shaft head, until the residues are deposited on the dump, the various products are conveyed from point to point either by water, moving under the influence of gravity, supplemented by sludge pumps, or by purely mechanical appliances. In other words, native labour has been practically eliminated from the surface operations of the City Deep Mine.

The Mill of the Brakpan Mines, Limited, East Rand.*—The ore is the usual Rand ore, and assays from 0·33 to 0·43 oz. gold per ton. The operations in outline are as follows :—

1. Coarse crushing with heavy stamps.
2. Classification and dewatering in cones.
3. Tube milling followed by amalgamation on plates.
4. Classification into sand and slime.
5. Collection and leaching of the sand.
6. Collection of the slime in settling vats.
7. Leaching in Brown vats (intermittent system).
8. Treatment in Butters' vacuum filters.
9. Precipitation with zinc dust in Merrill presses, after clarifying in sand filters.

A plan of the mill is given in Fig. 148.

There are 160 stamps, each weighing 2,004 lbs. Coarse screening is used, and all pulp flows directly to two coarse sand pumps, driven by motors, whence it is delivered to the launders, which distribute to the tube-mill cones. All tube-mill and battery launders conveying coarse sand are lined with asphalt.

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* *Eng. and Min. Journ.*, Oct. 1911.

The pulp is dewatered by Caldecott diaphragm cones to 27 per cent. of moisture, and passes to the tube mills, where the water is brought up to 35 per cent. There are six tube mills, each 5 feet 6 inches in diameter by 22 feet long, fitted with Schmitt feeders.

The tube mills discharge to a set of five stationary amalgamation plates, 12 × 5 feet.

From the plates the pulp flows to a pit, in which are a pair of pumps, and the sand is thus delivered to return cones, the finished overflow product from which goes to the cyanide plant, and the coarse underflow is returned to the two central tube mills for regrinding.

Sand Plant.—The finished overflow from the tube-mill return cones goes to the sand-collecting plant, where a set of cones is installed for delivering a sand product to the collectors, and a slime overflow to the slime launders.

From the sand collectors the material is conveyed by belts discharging to a main conveyor belt, by which it is carried to a Blaisdell distributor and discharged into the sand-treatment vats. Finally, after treatment, the sand is taken in bucket conveyors by the Bleichert system, or aërial haulage, extending from below the treatment vats to the extremity of a lofty cantilever, and discharged on the dump.

The Slime Plant.—From the sand collectors the overflow goes to a set of cones where the pulp joins the overflow from the sand cone, and where the last vestiges of sand are, as far as possible, eliminated and sent back to the collector cones. The slime goes to settling vats, whence it is transferred by centrifugal pumps to six Brown agitators, or Pachuca vats, 45 feet high by 15 feet diameter.

After four hours' agitation in the Brown agitators with 1·6 of solution to 1 of slime, the pulp is transferred to a stock-pulp vat, and eventually goes to the Butters vacuum filter plant.

The solution from the Butters filter is clarified through two sand filters, used alternatively, before being delivered to the gold solution storage, whence it is pumped to the Merrill presses, with the addition of zinc-dust emulsion. The zinc dust for this purpose is fed slowly by a belt feeder into emulsifying cones, where it is agitated with weak solution by means of a jet of air.

The presses have a capacity of 100 tons per day.

The Black Oak Mill, Tuolumne County, California.*—The ore is very hard, siliceous, fairly high grade, $20 per ton, and non-pyritic.

The operations consist of :—

1. Coarse crushing in cyanide solution with 1,250-lb. stamps.
2. Classification and dewatering the pulp.
3. Tube milling to slime by "closed circuit" system.
4. Thickening the slime in Dorr thickeners.
5. Leaching in Brown vats by the continuous system.
6. Thickening in Dorr thickeners.
7. The underflow going to an Oliver filter.
8. The overflow going to a clarifying press.
9. Precipitation of the solutions from 7 and 8 with zinc dust in Merrill presses.

A flow sheet of the mill is shown in Fig. 149.

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* *Min. and Sc. Press*, Nov. 1912.

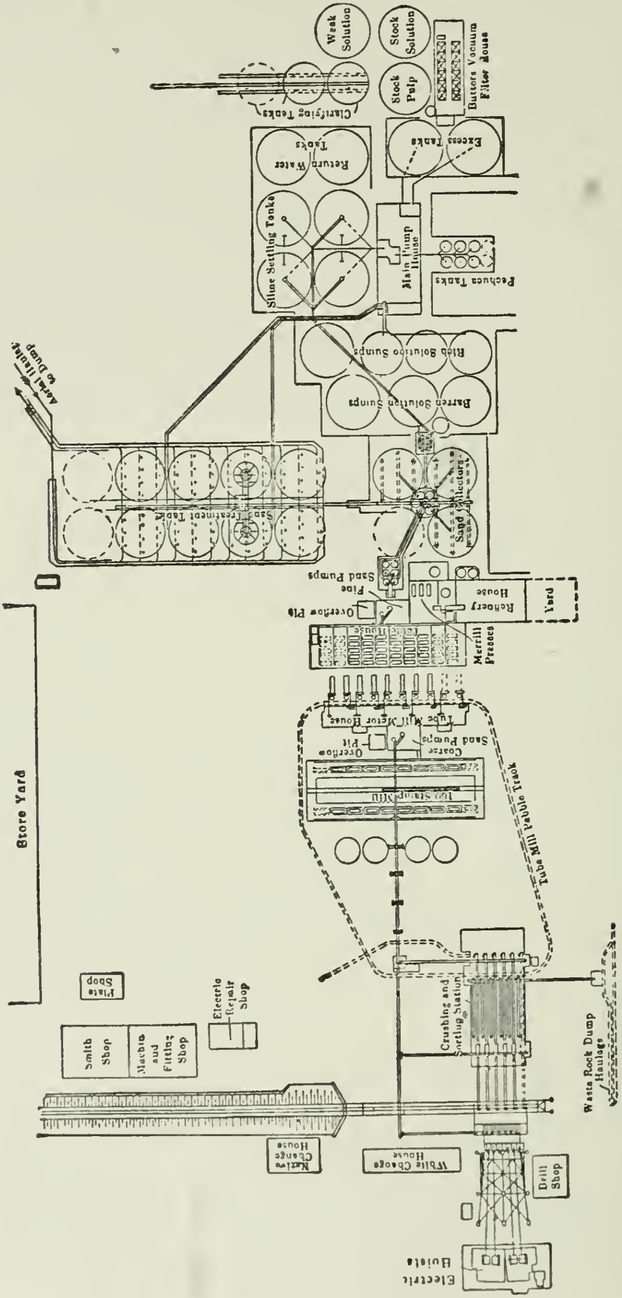
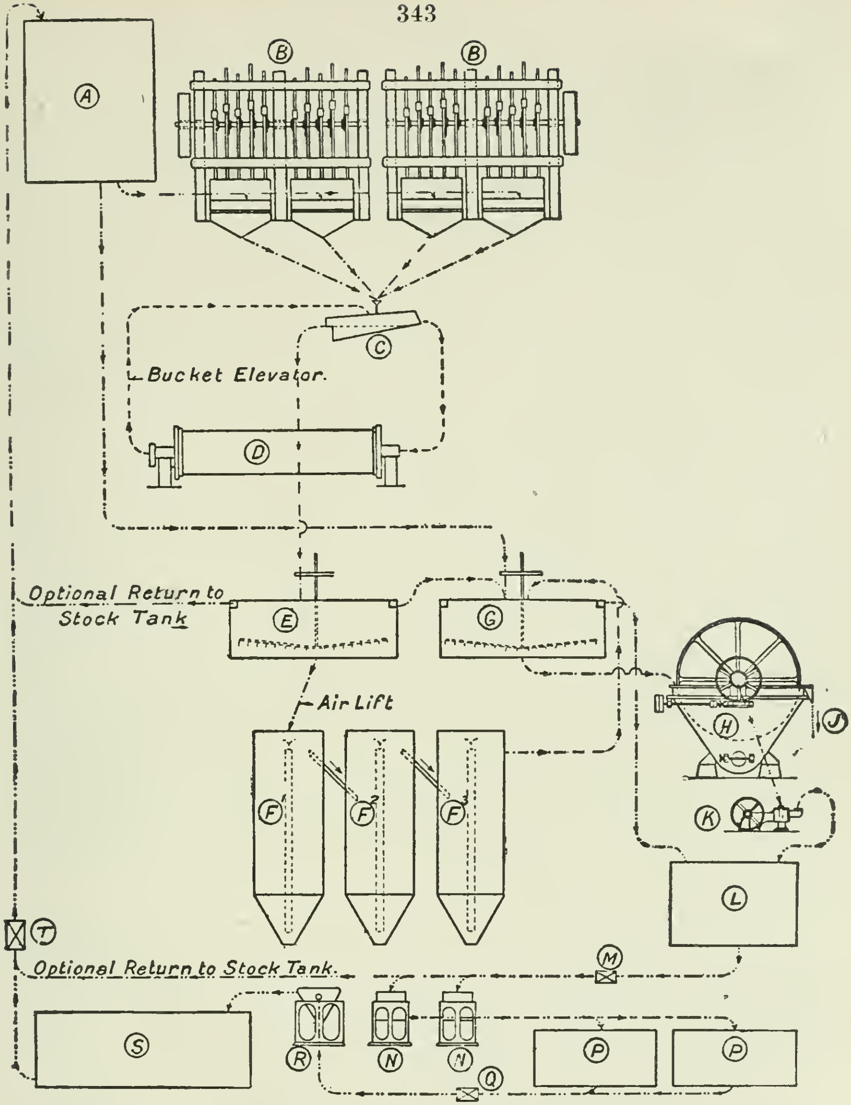

Weak Solution
Stock Solution
Stock Pulp
Butters Vacuum Filter House
Clarifying Tanks
Return Water Tanks
Excess Tanks
Slime Settling Tanks
Main Pump House
Pachuca Tanks
Rich Solution Sumps
Barren Solution Sumps
Aerial Haulage to Dump
Sand Treatment Tanks
Sand Collectors
Fine Sand Pumps
Overflow Pit
Refinery House
Yard
Merrill Presses
Tube Mill Motor House
Coarse Sand Pumps
Overflow Pit
100 Stamp Mill
Tube Mill Pebble Track
Store Yard
Plate Shop
Electric Repair Shop
Smith Shop
Machine and Fitting Shop
Crushing and Sorting Station
Waste Rock Dump Haulage
Native Change House
White Change House
Drill Shop
Electric Hoists

Fig. 148.—The Cyanide Plant at the Brakpan Mine. (*Eng. and Min. Journ.*, Oct. 1911.)


A
B
B
C
Bucket Elevator.
D
Optional Return to Stock Tank
E
G
Air Lift
H
J
F1
F2
F3
K
L
T
Optional Return to Stock Tank.
M
S
R
N
N
Q
P
P

A, Stock Tank (140 tons).
B, 20-Stamp Battery (1,250-lb. stamps).
C, Classifier (Dorr Duplex).
D, Tube Mill (5 × 18 ft.).
E, Dorr Thickener (20 × 10 ft.).
F, Pachuca Agitators (10 × 30 ft.).
G, Dorr Thickener (20 × 10 ft.).
H, Oliver Continuous Filter.
J, Filter Residue Discharge.
K, Vacuum Pump.
L, Collecting Tank.
M, Dow Duplex Pump (4 × 6 ins.).
N, Shriver Clarifying Presses.
P, Gold Tanks (15-ton).
Q, Dow Duplex Pump (4 × 6 ins.).
R, Merrill Precipitating Press.
S, Sump (70-ton).
T, Triplex Pump ($5\frac{1}{2}$ × 8 ins.).

Fig. 149.—Flow Sheet of Black Oak Mill.

The twenty stamps used in the old mill were light, 750 and 850 lbs., and have now been replaced by new stamps weighing 1,250 lbs.

The ore is crushed in cyanide solution, 3·7 lbs. per ton, through screens with openings equivalent to 10-mesh. The pulp passes to a Dorr classifier, from which the coarse material goes direct to the 5 by 18-foot tube mill, being diluted to 39 per cent. moisture. The slime overflow passes to the agitation plant. The discharge from the tube mill is returned to the classifier by a bucket elevator, so that the pulp must return to the tube mill until fine enough to escape at the slime end of the classifier; the usual closed-circuit arrangement.

The slime from the classifier goes to a 20 by 10-foot Dorr thickener, where it is thickened from a 6 to 1 consistence to 2 to 1 for agitation. The agitators are three in number, and of the Brown type, 10 by 30 feet, and connected for continuous agitation.

A spider, with six radiating jets, supplements the main working air jet as a help in starting at any time.

Having passed through the agitators, the pulp flows to another Dorr thickener, the same size as the first. The overflow from the thickener goes to a small collecting tank, as it is called, from which it is pumped to the clarification and precipitation presses. The thickened underflow passes to the filter.

The filter is an Oliver with a drum 11 feet 6 inches in diameter and 12-foot face.

In the continuous method of agitating and leaching in the Brown vats at this mill the vats are connected in the following manner:—There is a drop of 4 inches from vat to vat. In each vat a box about 1 foot square and 6 inches deep is fixed against the central air-lift tube, with its top slightly below that of the tube. Attached to the bottom of this box is a 4-inch tube, which passes through the side of the vat, about 3 feet below its edge, and connects with the adjacent vat. The pulp passes through these tubes, from vat to vat, the flow being regulated by a sliding cover on the top of the box in each vat.

For another arrangement for continuous treatment, see p. 406.

Hollinger Cyanide Mill, Porcupine, Ontario, Canada.*—Ore. Schist with one-third quartz. The general run of the ore milled has a value of about $20 per ton, of which about 98 per cent. is extracted in the mill.

Operations.—1. Crushing with 1,500-lb. stamps, through 6-mesh screens, in cyanide solution.

2. Classification of the tailing in Dorr classifiers into sand and slime.
3. Grinding the sand in tube mills, with "closed circuit."
4. Dewatering the slime from 2 and separating concentrate on tables.
5. Collecting the concentrate and amalgamating in pans.
6. Collecting, cleaning, and converting the amalgam into bullion in the usual way.
7. Thickening the tailing from 5 and treating it in agitation vats.
8. Filtering the pulp in Moore vacuum filters.
9. Clarifying the solutions in Merrill clarifying presses.
10. Precipitating the gold with zinc dust in Merrill presses.

The ore is broken to 2½-inch size, and is crushed in a battery of 40 stamps,

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* Megraw, *Eng. and Min. Journ.*, Dec. 1912.

1,500 lbs. each, through 6-mesh screens. The crushing is done in cyanide solution containing $1\frac{1}{2}$ lbs. KCy per ton. The pulp from the stamps is run to four Dorr classifiers, the sand from which is ground in four 5 by 20-foot tube-mills, the product being returned to the classifiers by the closed-circuit system until slimed.

The slime is dewatered in spitzkasten to a pulp, consisting of three of solution to one of solids, which is led to 40 concentrating tables.

The concentrate obtained is amalgamated in Wheeler pans in charges of $1\frac{1}{2}$ tons with 100 lbs. mercury and some lye for keeping the mercury clean, the pan being filled up with cyanide solution. The time required for amalgamation is four hours. The amalgam is collected and cleaned in the usual way in settlers and clean-up pans, and retorted. The tailing from the concentrating tables and the pulp from the amalgamating pans are delivered to four Dorr thickeners, lime being added as they pass in. The pulp then goes to the agitation vats, of which there are four, each 30 by 15 feet, of the Trent type. It is treated continuously through three of these vats, the fourth being kept in reserve. The solution used contains $1\frac{1}{2}$ lbs. KCy per ton—*i.e.*, the same strength as that used throughout the mill.

The pulp after treatment is sent to the Moore filter plant, and the gold solution from the filters, after passing through two Merrill filter presses, is precipitated with zinc dust in a Merrill press. Some cyanide is added to the gold solution before precipitation. The precipitate is melted in crucibles with borax, soda, and sand, the gold sponge from the amalgam being added.

The bullion obtained is 760 fine.

As the Trent agitators have not been found as satisfactory for this ore as was expected, experiments are now being made with agitators of the Dorr type.

The amalgamation of the concentrate will also be relinquished, and treatment with cyanide alone substituted.

The Porcupine Crown Mill, Ontario, Canada.—A method of continuous decantation, termed *counter-current* decantation, has been introduced in some of the new cyanide plants in America. It consists in treating the pulp from a system of agitators by dilution and transference through a series of Dorr thickeners.

The procedure will be readily understood from the following description by Mr. H. A. Megraw of the practice at the new mill of the Porcupine Crown Mines Company, Ontario.* The closed-circuit system is employed for the treatment of the ore, cyanide being added in the usual way. The flow sheet of the mill is given in Fig. 150.

" The ore from the mine is passed over a grizzly, which by-passes the fines around a gyratory crusher, the oversize of the grizzly going to the crusher.

" A bucket elevator elevates this ore and delivers it to a belt conveyor, which places it in a 270-ton ore bin at the mill head.

" Twenty 1,050-lb. stamps are installed to crush the ore, and these deliver the pulp to two Dorr classifiers.

" The product of the two tube mills goes directly to the amalgamating plates and the tailing from the plates is sent back to the classifiers again, so that any sand which is oversize is taken out by the classifiers and returned

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* Megraw, *Eng. and Min. Journ.*, Sept. 1916.

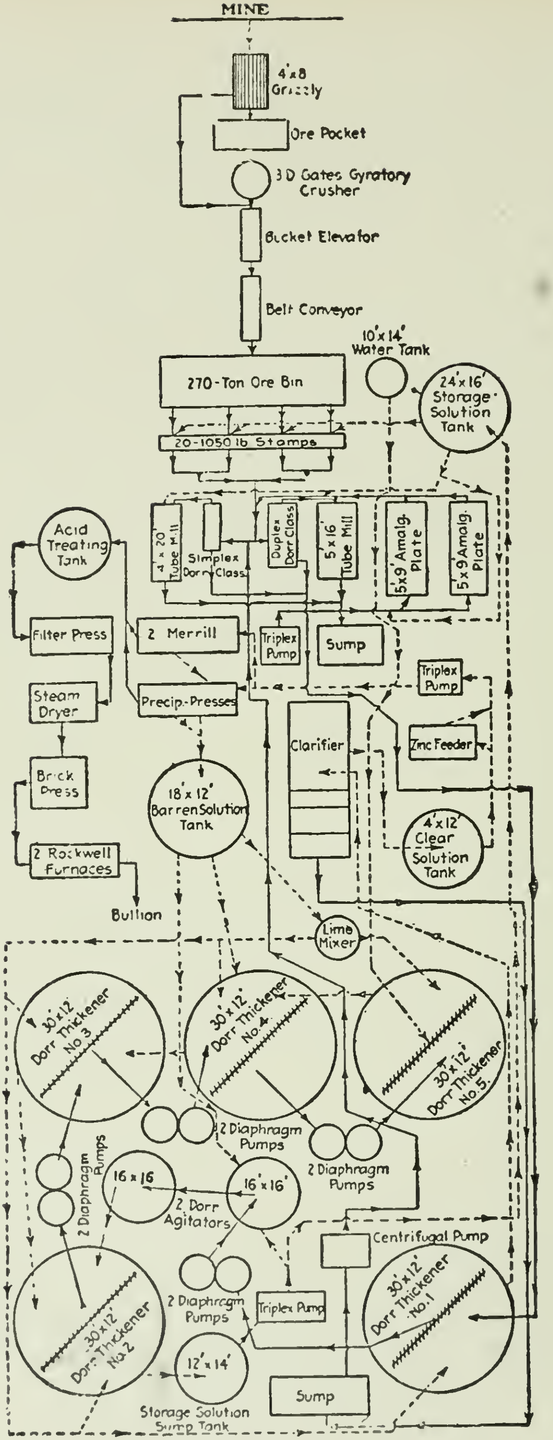
MINE
4'x8 Grizzly
Ore Pocket
3 D Gates Gyratory Crusher
Bucket Elevator
Belt Conveyor
10'x14' Water Tank
24'x16' Storage Solution Tank
270-Ton Ore Bin
20-1050 lb Stamps
Acid Treating Tank
4'x20' Tube Mill
Simplex Dorr Class.
Duplex Dorr Class.
5'x16' Tube Mill
5'x9' Amalg. Plate
5'x9' Amalg. Plate
Filter Press
2 Merrill
Triplex Pump
Sump
Triplex Pump
Steam Dryer
Precip.-Presses
Clarifier
Zinc Feeder
Brick Press
18'x12' Barren Solution Tank
4'x12' Clear Solution Tank
2 Rockwell Furnaces
Bullion
Lime Mixer
30'x12' Dorr Thickener No. 3
30'x12' Dorr Thickener No. 4
30'x12' Dorr Thickener No. 5
2 Diaphragm Pumps
2 Diaphragm Pumps
2 Diaphragm Pumps
16x16
16'x16'
2 Dorr Agitators
Centrifugal Pump
2 Diaphragm Pumps
Triplex Pump
30'x12' Dorr Thickener No. 1
30'x12' Dorr Thickener No. 2
12'x14'
Storage Solution Sump Tank
Sump

Fig. 150.—Flow Sheet, Porcupine Crown Mill.

to the tube mills for further grinding. In this way it may be said that the classifiers, tube mills, and amalgamating plates are in a closed circuit, from which nothing can find outlet unless it is fine enough to be considered as slime and treated as such. The combined slimes from the two classifiers are taken through the first Dorr thickener (p. 307), which is 30 feet in diameter and 12 feet deep.

"The overflow from this thickener is taken to a clarifier, which is built on the leaf-filter principle, the clear solution going to a 14 by 12-foot tank, whence it is extracted by a triplex pump having a zinc feeder in the suction, which delivers to two Merrill precipitating presses.

"The counter-current decantation is carried on as follows:—The underflow from the first thickener is elevated by a diaphragm pump to a Dorr agitator (p. 314), 16 by 16 feet, where the pulp receives agitation and proceeds continuously through another identical agitator. These two machines give the pulp all the agitation it needs and recover an economically satisfactory proportion of the gold in solution. It is true that in the further progress of the pulp through the thickeners, which wash and clean the pulp, a slight further extraction is secured, but its extent can be forecasted with great accuracy, and is without doubt the cheapest way of securing it. While in the agitators cyanide is added to bring the strength up to the required mill standard. From the second agitator, the pulp goes to another Dorr thickener, known as No. 2. This is also a 30 by 12-foot machine, identical in size with No. 1. Its overflow is led to a 12 by 14-foot solution storage tank, from whence it is pumped either back to the first agitator or to the solution storage tank, which is a 24 by 16-foot tank, situated in the upper part of the mill, and feeds by gravity to the stamp battery. A small lime-mixing barrel is charged with lime, fed with barren solution from the barren-solution tank, and led to all the thickeners, so that alkalinity can be applied at any point, or all points, whenever required.

"The underflow from the Dorr thickener No. 2 is received in diaphragm pumps and elevated to thickener No. 3. The overflow from thickener No. 3 goes back to dilute the inflow into the thickener No. 2. The underflow from thickener No. 3 goes to thickener No. 4, whose overflow goes back to dilute the inflow into thickener No. 3. Thickener No. 4 underflows to thickener No. 5, its overflow going back into No. 4. The thick pulp inflow to thickener No. 5 is barren solution from the tank which receives the precipitated solution from the Merrill filters. In this way it will be seen that, beginning with the final one, which receives barren solution, the overflow of each thickener in succession proceeds to dilute the thick pulp inflow of the preceding one. Thus, the procedure is from the last thickener of the series back to the first, dilution always being with weaker solution than that with which the pulp enters.

"The final outflow from the final thickener is discarded without any filtering.

"The thick pulp underflow from each of the Dorr thickeners installed in the mill circuit contains from 30 to 40 per cent. of moisture. By careful manipulation and close watching the underflow may be kept continuously at very nearly 30 per cent. of moisture. It will be readily seen and understood that by successive dilution (with barren solution where necessary) and thickening of this kind, practically all the gold-bearing solution may be displaced by weak, low-gold solution, a small portion of which may be discarded with impunity. This obviates the large installation expense attendant upon filter installations, and also the operating cost of such machines."

Water equal in amount to the solution leaving with the pulp as tailing is sometimes used for dilution in the last thickener.

A point of interest is that the overflow solution from the first thickener is the only one precipitated. The barren solution from precipitation goes to dilute the inflow into the second thickener, the overflow from which goes back into the first, and so on.

The United Eastern Mill, at Oatman, Ariz.*—" The milling process consists of single-stage coarse crushing, two-stage ball milling in cyanide solution, followed by combined mechanical and air agitation, and by straight counter-current decantation.

" The Merrill zinc-dust precipitation method is used to recover the valuable constitutents of the ore, and is preceded by the Crowe vacuum treatment of the solution."

The ore is first crushed in a rock-breaker, which delivers a 2-inch product to an ore bin by means of a belt. From this bin the ore, with the addition of lime, is fed to a Marcy mill, working in closed circuit with a Simplex Dorr classifier. This mill carries a load of 9,000 lbs. of 5-inch forged chrome steel balls. It reduces 260 tons of—2-inch ore to—20 mesh. The grinding is carried on in a 1·6-lb. per ton KCy solution, containing 1 lb. per ton of protective alkali (lime).

Fine grinding is done in two 5 feet by 6 feet ball mills. These mills carry a ball load of 8,000 lbs. of 2-inch chrome steel balls. They grind about 90 tons each from—20 mesh to 82 per cent.—200 mesh, working in closed circuit with a duplex 54-inch Dorr classifier and an 8-foot Callow cone. The spigot product is returned by a pump to the classifier.

From the fine grinding department, the pulp flows by gravity to a No. 1 Dorr thickener, the thickened underflow from which is pumped to the first of a series of seven Dorr agitators 14 feet by 24 feet in diameter. The period of agitation being about sixty-two hours.

From the agitators the pulp flows through five 40-feet Dorr thickeners arranged for straight counter-current decantation. The pregnant solutions from the primary thickener flows to the No. 1 gold tank, from which it is pumped through a Merrill clarifying filter. This filter delivers the clear solution to the No. 2 gold tank, or steady-head tank of the Crowe vacuum treatment system.

Vacuum treatment is carried out in a 4-foot by 10-foot vacuum receiver or drum set on end, the inlet of which is in the centre of the top and 23·4 feet above the solution level in the steady-head tank. The solution is poured down over a series of perforated trays. During this process, the occluded air is liberated and removed by the vacuum pump. The solution from the vacuum receiver is fed to a pump, where it is mixed with zinc dust and pumped to the Merrill presses. The barren solution is returned to the No. 4 thickener.

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* W. O. North, Chicago Meeting of the A.I.M.E. (*Eng. and Min. Journ.*, October, 1919).

The undried precipitate after the moisture content has been determined is melted in a crucible in an oil-fired tilting furnace, with 11 per cent. borax glass, $11\frac{1}{2}$ per cent. sodium bicarbonate, 6 per cent. manganese dioxide, 3·3 per cent. ground bottle glass, and 10 per cent. of old slag shells from previous melts, the percentages being in terms of the calculated weight of the dry precipitate.

The Treatment of Sulpho-Telluride Ores.—These ores are of extensive occurrence in the Kalgoorlie district of West Australia, and in the Cripple Creek district, Colorado, U.S.

On account of the presence of tellurium with which gold is combined in the minerals described on p. 254, it cannot be extracted by treatment with cyanide without previous roasting, or without the use of cyanogen bromide, BrCy, together with potassium or sodium cyanide.

In West Australia the ores contain from 7 to 13 per cent. calcite, 4 to 8 per cent. magnesium carbonate, 7 to 10 per cent. iron pyrites, the remainder being chiefly quartz and aluminium silicate. The tellurium present ranges from 0·03 to 0·15 per cent. (*Rose*).

Two methods of treatment are followed—viz., the "Marriner process" and the "Diehl process"—both so named after their respective originators. Both processes are in successful operation, but, according to Alfred James, the former is at present giving the most profitable extraction.

In the dry-crushing plants, ball or Griffin mills are employed instead of stamps. In those using wet crushing, stamps are used, and the crushing is done in cyanide solution.

The All-Roasting and Sliming Process, termed the "Marriner" Process.—This process is practised at the Great Boulder Perseverance, Great Boulder Proprietary, the Kalgoorlie, and other mines, the operations being as follows:—

1. Dry crushing in Gates or Blake rock breakers, followed by ball mills or Griffin mills.
2. Roasting the product dead in Edwards, Merton, or other furnaces to oxidize sulphides and tellurides, the gold being thus rendered susceptible to amalgamation and extraction by cyanide solutions. The roasted ore is then conveyed by a stream of weak cyanide solution to spitzkasten.
3. In the spitzkasten it is separated into sand and slime, the sand going to Wheeler pans, and the slime to agitation vats.
4. In the Wheeler pans the sand is ground fine, and mercury being charged in, some gold is obtained by amalgamation. The continuous overflow from the pans is again treated by spitzkasten and separated into sand and slime, the former being returned to the pans, and the latter sent to the agitation vats.
5. The agitation vats are 21 feet diameter and 6 feet deep, and are provided with stirrers revolved by bevel gearing. Cyanide is added, to bring the strength of the solution to 0·1 per cent. KCy, and the pulp is agitated for about eight hours.
6. The pulp is then drawn off into montejus or pumps and forced into filter presses, the issuing gold solutions being passed through another filter

press to clarify them, and then to the zinc boxes for the precipitation of the gold.

The yield of gold is from about 90 to 94 per cent. of that contained in the ore.

Roasting at the Great Boulder Perseverance is conducted in furnaces in which the Edwards system and the Holtoff Wethey system are combined, the former system of rabbling being adopted on the top, or roasting hearth, and the latter on the lower or cooling hearth.

The pans in use generally in West Australia are of the Wheeler type. They range in size from 5 to 8 feet in diameter, the former size requiring 4½ to 6½ H.P., and revolving about 55 to 60 turns per minute, and the latter 6 to 10 H.P., with 27 to 33 revolutions. At some mills, as the shoes lose weight and their grinding power is thus lessened, one or two cast-iron rings, of about as much as 600 lbs. each, are put over the yoke to compensate for this loss. A new modification of the Wheeler pan has been introduced by Messrs. Cobbe and Middleton, in which the pressure between the shoes and dies is maintained constant by means of weighted levers acting below the body of the pan and pressing it upwards. The body of the pan is held by guides, up and down which it can slide, and it can be depressed, without stopping the muller, when it is desired to release the pressure, by a hand wheel at the side.

At the Great Boulder Perseverance the addition of lead acetate, about 1 lb. per 5 tons of ore, to the slime in the agitation vats has been found beneficial, and to increase the extraction of the gold, and especially of the silver.

The Diehl Process, as employed at the Oroya-Brownhill Mine.*—The ore, after being crushed in a rock breaker, is conveyed to the stamps.

1. At the stamps the ore is crushed in weak cyanide solution, containing about 0·04 per cent. KCy, kept alkaline by the addition of lime, and the pulp is run direct to spitzkasten.

2. The spitzkasten separate the sand from the slime. The sand goes to Wheeler pans, and the slime to other spitzkasten, where it is again classified, and the coarse returned to the pans.

3. At the Wheeler pans the sands are ground without mercury, and the product is passed over Wilfley tables.

4. The Wilfley tables separate concentrate, which receives special treatment. The tailing is sent to classifiers, the coarse pulp from which is delivered to tube mills to be slimed, and the fine to Wilfley tables to further separate concentrate.

5. In the tube mills the pulp is slimed in the usual manner and also sent to classifiers, the coarse being returned to the mills.

6. The whole of the slime separated by the varying classifiers is thickened in spitzkasten, and then goes to the agitation vats.

7. The agitation vats are from 20 to 25 feet in diameter and from 7 feet 6 inches to 8 feet deep.

The pulp is agitated with mechanical stirrers, with cyanide solution containing 0·1 per cent. KCy, first for three hours, then cyanogen bromide is added, about 1 lb. for each ounce of gold, and the agitation is continued for another 12 hours. About two hours before the completion of the agitation lime to the amount of 2 to 3 lbs. per ton is added. After agitation the pulp is discharged into a sunken agitator, whence it is pumped by a plunger pump into filter presses.

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* *Trans. Inst. of Min. and Met.*, vol. xii. (1902), p. 1.

8. The gold-bearing solution issuing from the presses is passed through other presses for clarification, and thence to the zinc boxes. The concentrate is treated as described on p. 353. All the residues are discharged on to belt conveyors, by which they are carried to the dump.

In three months in 1905 the ore contained 31·32 dwts. gold per ton of 2,000 lbs., and of this 94·6 to 95 per cent. was extracted.

At Cripple Creek the ores are altered andesite, granite, or phonolite, containing thinly disseminated iron pyrites, and tellurium minerals mostly calaverite, associated with quartz and often with fluorite (*Argall*).

Until recently they were treated by chlorination, and also by roasting, followed by cyaniding. The former process has been entirely abandoned, and the latter is being replaced by concentration and cyaniding the tailing. The practice at the Stratton's Independence,* one of the most important mines, is as follows :—

1. The ore is broken in gyratory crushers to less than 2-inch cubes.
2. To the broken ore lime is added ; it is then moistened with cyanide solution, and ground by rolls to about $\frac{1}{4}$-inch size.
3. From the rolls it passes to Chilian mills, in which it is ground to pass a screen having an aperture of 0·046 inch. The milling is done in cyanide solution containing $\frac{1}{2}$ lb. KCy per ton.
4. The product from the mill is led to classifiers, the sand from which goes to concentrators (card type), the slime to the slime concentration department.
5. At the sand concentrators a high-grade concentrate is produced, which is shipped direct, and a middling, which is reground and reconcentrated
6. The slime from the classifiers is thickened in cones, and treated on concentrating tables (Deister's preferred), where it is concentrated as much as possible.
7. The tailing from 6 is cyanided. See 10.
8. The sand tailing from 5 is treated in classifiers to separate slime, and is charged into sand vats.
9. In the sand vats it is treated with $\frac{1}{2}$ lb. cyanide solution, and is then sluiced out.
10. The slime from 6 and 8, after thickening, is pumped into a vat, where it is agitated with $\frac{3}{4}$ lb. cyanide solution for six hours, and afterwards with cyanogen bromide for four hours in a separate vat.
11. The pulp from 10 is fed into a storage tank, and thence goes to a Butters filter.
12. The gold solutions are precipitated with zinc shavings in the usual manner, and the precipitate is shipped to smelters.

The extraction is 71·5 per cent., of which 43·65 per cent. is obtained by concentration and 27·85 by cyaniding.

The average content of the ore treated has a value of only about $3·50 per ton, as milled, and it is due to Philip Argall that the working of such a poor ore is being carried out with profit.

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* Megraw, *Eng. and Min. Journ.*, Feb. 1913.

Treatment of Gold Ore in which Associated Carbonaceous Schist prematurely precipitated part of the Gold dissolved by the Cyanide Solution.*—The process is practised at the Prestea Mine, Gold Coast, West Africa. The gold occurs in quartz seamed with carbonaceous schist, and is associated with iron pyrites, arsenical and antimonial sulphides.

The operations are as follows:—The ore is crushed and ground with stamps and grinding pans. Amalgamable gold from the raw ore is recovered by the concentrating action of the grinding pans and subsequent pan amalgamation, also by collecting on blankets and subsequent barrel amalgamation, and by direct pan amalgamation.

Wilfley table concentration is practised to separate mineral sulphides. The concentrate is roasted, ground and amalgamated in pans, and cyanided. Of the concentrate tailing classified into sand and slime, the sand is cyanided and then treated with the sodium sulphide process.

A 240-ton sand charge is treated with strong and medium cyanide solution and allowed to drain thoroughly. The charge is then leached with 60 to 70 tons of sodium sulphide solution ·20 per cent. strength, followed by 100 tons of water-wash; the vat is then drained dry and discharged. The gold brought into solution by the Na_2S is immune from precipitation by carbonaceous schist.

The precipitation of the gold is effected by passing the effluent Na_2S solution through boxes filled with copper shavings. For the clean-up the contents of the boxes are washed and the fines pumped to a settling tank, filter-pressed, and dried. The coarser precipitate with short copper is dried and screened through a 14-mesh screen returning all plus 14-mesh to the boxes. The dried and screened precipitates are mixed and roasted in a muffle until most of the CuS is converted into CuO. The roasted precipitate is sold for its gold and copper content. The increase in extraction due to the sodium sulphide leaching averages two shillings per ton of sand, with a consumption of sulphide of 1·2 lbs. An alloy of 25 per cent. aluminium and 75 per cent. zinc was found to be far superior to copper as a precipitant for gold, and will be used as soon as market conditions permit.

Treatment of Concentrate.—In gold and silver ores, containing pyrites, the precious metals are often present in the pyrites in amounts which can be extracted with profit. In some cases, indeed, it is the most valuable part of the ore, and occasionally may be the only part of value, but generally the gold and silver are present in the whole of the ore.

When the pyrites is the only rich constituent and the gangue is too poor to be worth treating, it may be separated by concentration on suitable vanners, the gangue being rejected. In other cases the whole of the ore must be treated, and it then becomes important to decide whether the ore shall be treated as a whole, or shall the pyrites be separated by concentration, and it and the pulp be subjected to separate treatment. At several mills the latter is found to be best, and it has this advantage that the pyritic matter, which is liable to foul the cyanide solutions, is removed at an early stage, and the cyaniding of the pulp is facilitated.

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* F Wartenweiler, *Trans. Inst. Min. and Met.*, vol. xxvii., p. 372.

Further, as a longer time and stronger cyanide solutions are required for the maximum extraction of gold, and especially of silver, from pyrites than from the quartzose pulp, of which the ore chiefly consists, a separate treatment of the concentrate may sometimes be advisable. At other mills it has been found to be more profitable to cyanide the whole of the ore after grinding it to slime.

Formerly the concentrate was always shipped to smelters or chlorination works, but, since it has been found that it will yield its gold or silver to cyanide solutions, it is now being treated at several mines.

No standard method for its treatment has yet been or can be decided on, as it must vary with the nature of the concentrate and the mode of occurrence of the gold and silver in it, the practice hence differs at almost every mill. The solutions used range from 0·4 to 0·6 per cent. KCy, and agitation is generally practised, as percolation is difficult unless the concentrate is mixed with sand.

In many cases a dead roast, before cyaniding, will give a much higher extraction in a given time than when the concentrate is treated raw, and this is the common practice in West Australia.

The following is the practice at three important mills :—

The Waihi Mine, New Zealand.—At this mine the ore is crushed in cyanide solution. The pulp from the stamp batteries flows to classifiers, the underflow from which passes to tube mills, then to other classifiers, the coarse being returned to the tube mills. The slime overflow from these classifiers passes over amalgamation plates, then to vanners and Wilfley tables.

The concentrate from these is treated as follows, an extraction of 96·3 per cent. of the gold and 93·5 per cent. of the silver being obtained :—

" The concentrate consists chiefly of iron sulphide with a small proportion of zinc, copper, and lead sulphides ; it is shovelled from the collecting boxes into tubs holding about 600 lbs. wet weight. Care is taken to keep the concentrate under water.

" Some 500 tons are produced each month, assaying about 5·5 ozs. gold and 65 ozs. silver per ton. The concentrate is ground in tube mills and delivered to spitzkasten, the coarse being returned to the tube mills and the fine passing to dewatering boxes.

" Slaked lime is added in amount equal to 10 lbs. per ton. Agitation by air is carried out in conical-bottom tall tanks, 16 feet by 6 feet, the solution being kept at an average strength equal to 0·4 per cent. KCy. The time of agitation varies from 8 to 10 days.

" The solution is then separated by filter-pressing, and the bullion is precipitated by zinc filament. Consumption of the sodium cyanide which is used averages 16 lbs. per ton ; this represents 0·25 lb. per ton of original ore." *

Oroya-Brownhill Gold Mines, West Australia,† 1906.—The concentrate from the Wilfley tables, amounting to 6 per cent. of the ore milled, contains about 11 ozs. of gold per ton, and the great bulk of the refractory elements in the ore. The elimination of the latter is important, in order to avoid excessive consumption of chemicals in the raw slime agitation vats.

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* E. G. Banks, *Min. and Sc. Press*, January, 1911.

† *West Australian Metallurgical Practice*, pp. 20 to 24

The concentrate is sent to three Merton furnaces, in which it is roasted with salt, about ½ lb. to 2 lbs. per ton. These furnaces easily roast 10 tons of concentrate each per twenty-four hours, the duration of the roast being five hours.

The roasted product is removed by a push conveyor to two pairs of 5-foot Wheeler pans, worked in parallel. The first pair is used both for fine grinding and amalgamation, their overflows passing on to the second pair, which is used for fine grinding only. Mercury is added three times daily to the first two pans, amalgamation recovering about 30 per cent. of the value of the concentrate.

The ground pulp is elevated by a plunger pump to a pair of spitzkasten, which eliminate any coarse material for returning to the second pair of grinding pans.

The overflow from the pans is agitated in vats with mechanical agitators with ordinary cyanide solution, 0·1 per cent. KCy, for 100 hours, lime and lead acetate having been sometimes added in the pans. The pulp is afterwards filter-pressed. The gold-bearing solutions are precipitated in ordinary extractor boxes containing zinc shavings which have been dipped in lead acetate solution.

The Goldfield Consolidated Mill, Goldfield, Nevada.*—The ore is slimed in tube mills before concentration. About 40 to 50 tons of concentrate, containing 6·50 ozs. gold per ton, is produced daily. An extraction of about 81 per cent. of the gold is obtained.

The concentrate is sent to the concentration-treatment plant, where it is treated as follows:—It is collected in flat-bottom agitation vats, where it is neutralized with lime. From these it is pumped to Brown vats, in which it is agitated, during five periods of eight hours each, with cyanide solution containing 2 lbs. KCy per ton and lead acetate 1 lb. per ton of concentrate.

After each period decantation is practised, and the charge is re-agitated with fresh solution. This treatment with cyanide, which removes 80 to 85 per cent. of the gold, is followed for the purpose of reducing the value of the material to be roasted, in order to minimize the loss by dusting.

The pulp is filter-pressed, and the excess of moisture removed in the press.

It is then roasted in Edwards furnaces, 112 by 13 feet (see p. 29), and the product is cooled in a Baker cooler. This is a sheet-iron cylinder, 22 feet long and 5 feet in diameter, carried at each end on a hollow trunnion through which the ore is fed and discharged. It revolves with about 40° submergence in a water-tight concrete sump containing water.

After cooling, the ore is delivered into a sump, mixed with water, and elevated to a collecting and agitating tank, 20 by 12 feet, in which it is agitated for eight hours with sulphuric acid, 20 lbs. for each ton of concentrate. The acid liquor is run off, the pulp washed with water, and neutralized with lime. It is then agitated in Brown vats for a period of eight hours in a 2-lb. cyanide solution containing 1·2 lb. CaO. Five periods of agitation are given, each followed by decantation. The settled charge is delivered to a storage tank, and thence to a tube mill, where it is ground until 95 per cent. will pass a 200-mesh screen. It is then sent to the filter department, filtered, and the gold is precipitated by zinc dust.

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* *Min. and Sc. Press*, January and February, 1913.

The treatment with sulphuric acid has been found necessary, owing to the gold being coated with a film of oxides of Sb, Bi, Te, and Se, not removed in roasting, which hinders the action of the cyanide solutions.

Flotation *versus* **Cyanidation.**—The following is chiefly an abstract of an extremely important paper on this subject by G. H. Clevenger:*—Flotation has not been so successful in the treatment of precious metal ores as in that of copper and lead ores. In the case of the latter the extraction was increased by flotation at a reasonable cost, and from the concentrate the metal could be obtained by the same methods that were previously used. On the other hand, the cyanide process which had been developed for the treatment of siliceous gold and silver ores was giving extractions of from 90 to 99 per cent., and, in addition, the precious metals were produced in the form of bullion. Thus the field for flotation is somewhat restricted owing to this high efficiency of the older process, and moreover has the distinct disadvantage that it does not produce bullion, but a crude product (concentrate) not so satisfactorily marketed as bullion. As regards the cost of treatment by the two processes, if the same extraction could be obtained by each there is an advantage in favour of flotation in that its installation cost is considerably lower than is the case with the cyanide plant. There is, too, a further advantage that the cost of the treatment by flotation would be less in most cases than that of treatment by cyanide, and particularly so at present, with the high costs of all mill supplies. If, however, local treatment of the concentrate is practised, the additional cost of such a plant may tend to equalize the total plant cost. As a matter of fact, the majority of ores that are now being treated by cyanidation are giving better extractions than could be obtained by flotation. On the other hand, there are ores or tailings which are not readily amenable to cyanidation, and on which flotation will give good extractions. For example, the amalgamation tailing of the Mother Lode (California) mines give very poor extraction by cyanidation, but good extraction with flotation. Again, in the case of ores which give a good extraction by cyanidation, but where the tailing still contains sufficient gold and silver to render its further treatment desirable, flotation would seem to present promising possibilities.

In cases of ores containing base metals or other interfering elements, flotation might precede cyanidation for their recovery, as well as to eliminate their effect upon cyanidation. Indeed, in case of such ores, it frequently would happen that the gold and silver would be removed with the concentrate containing the base metals, when cyanidation would be superfluous.

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* *Eng. and Min. Journ.*, April, 1918, pp. 743, *et seq*

On the other hand, two well-known companies, one in the Goldfield (Nevada) and another in the Cripple Creek district, after giving up cyanidation for flotation, after a number of months went back to cyanidation.

GOLD REFINING.

The gold bullion obtained from stamp milling, cyaniding, and other processes always, with but rare exceptions, contains silver and more or less impurities, it is hence necessary that these should be removed, otherwise the metal is unfit for coinage and industrial uses. The gold must be refined.

The processes by which the metal is refined are chiefly as follows :—

1. Parting by nitric acid.
2. Parting by sulphuric acid.
3. Refining and parting by chlorine.
4. Parting and refining by electrolysis.
    - (*a*) The Moebius process.
    - (*b*) The U.S. Mint silver nitrate process.
    - (*c*) The Wohlwill process.

The gold bullion produced at mines, more particularly where the cyanide process is practised, is liable to be so low in fineness that the charges for refining when it is sold are exceptionally heavy. In this connection the following note by the late Arthur C. Claudet* is of special importance :—

"It is in the interest of mining companies exporting gold to endeavour to raise the fineness of the bars as much as possible, due attention being paid to economy in the operation.

"To accomplish this it is recommended that bars from the cyanide process assaying below 800 fine be remelted in clay pots, capable of holding 1,000 to 2,000 ozs. of metal ; nitre (nitrate of soda) to be added to the molten bullion, the metal to be stirred up, and the nitre to be removed by skimming. Successive quantities of nitre should be added and skimmed until the nitre is colourless. The metal should then be poured into moulds capable of holding about 500 ozs. This operation is technically called "toughening," and the cost of the operation of remelting and toughening should not exceed one-eighth to one-fourth of a penny per oz. of bullion. The nitre slags can be dissolved and the gold collected from the residues, or can be remelted, or used in melting the cyanide precipitate in the first instance."

If the bullion is very impure the following method, devised by Sir T. K. Rose, of the Royal Mint,† is most effective, and is specially suitable for the metal from cyanide mills. By its use, metal only 500 fine can be converted into bullion 990 fine in gold and silver in an hour or two.

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* Bulletin No. 2, *Inst. Min. and Met.*, 1904, p. 8.

† *Trans. Inst. Min. and Met.*, April, 1905.

The method consists in passing a stream of air or oxygen through molten bullion in clay pots by means of clay pipes similar to those used in Miller's chlorine process. The base metals are oxidized successively in the order, zinc, iron, antimony, arsenic, lead, bismuth, nickel, tellurium, copper. The oxidation of these metals, however, proceeds to some extent simultaneously, some copper being oxidized before the last traces of zinc are eliminated from the bullion. The oxides rise to the surface of the metal, and are slagged off with a mixture of borax and sand. Four parts of sand and 3 parts of borax are enough for slagging off about 6 parts by weight of base metals.

The end of the operation is difficult to determine, except by measuring the air passed through, or by dipping out part of the metal, casting it, and bending the ingot. If it is tough, only gold, silver, and copper remain unoxidized. If the operation is stopped as soon as the metal is tough, the losses of silver in the slag are small. The losses of gold in the slag are insignificant.

This method is used at the Mint to toughen brittle standard gold.

Separation of Osmiridium.—Osmiridium, which occurs as pale steel-grey coloured grains in the gold dust from some localities, will be found at the bottom of the bars or ingots obtained by melting the dust. Its presence is easily detected; in fact, it may occasionally be even visible in the form of unaltered grains on the bottom of the bars, as it does not alloy with gold. In other cases, on hammering the assay piece, cut from one of the lower edges, both the hammer and the anvil will be marked with rough patches owing to the hardness of the grains. In assaying such gold the cornet will have black, sooty spots or streaks on its surface.

In order to separate it from the bullion advantage is taken of its insolubility in molten gold, its high specific gravity, and its infusibility at ordinary furnace temperatures. The method adopted by the author in the Imperial Mint, Japan, where parcels of gold dust containing it were occasionally received, was as follows:—The gold dust was melted in a deep, narrow, conical clay crucible, and after careful stirring occasionally to prevent any osmiridium from settling on the sides, it was kept molten for an hour or more, the fire being then allowed to burn down. When the metal had solidified and cooled, the crucible was broken off from it. All the osmiridium was then found to have accumulated at the bottom of the cone. This was cut off and the osmiridium which was mixed with a little gold was separated by treatment with nitrohydrochloric acid. The method gave perfectly satisfactory results.

In America this so-called "settle-melting" is similarly carried out, but the gold is first alloyed with two or three times its weight of silver.

Gold and Silver Parting—*Parting.*—Parting is the separation of silver from gold, in order to obtain each metal in a commercially pure state.

In all the processes the base metals which are present in the bullion are separated from both the gold and the silver.

Copper and other base metals when present to the extent of more than 10 per cent. in bullion interfere seriously when sulphuric or nitric acid is used, but to a less extent in the latter case. They must, therefore, be first reduced to this or a lesser amount before such bullion is parted.

This may usually be accomplished by melting the bullion in a clay crucible and exposing it to the action of a blast of air or of fluxes, such as nitre and borax, and stirring well.

Parting by Nitric Acid.—The parting alloy at the Philadelphia Mint consisted of 2$\frac{1}{3}$ parts of silver and 1 part of gold. In many refineries the proportion of silver was less, the minimum being 1$\frac{3}{4}$ to 1 (*Rose*). The process, which is now obsolete, was as follows:—

The alloy is first granulated by melting and pouring it in a thin stream into water contained in a wooden tub. The tub has a removable copper lining, and contains a copper tray, with perforated sides, for receiving the granulations.

The boilers in which the granulations are heated with acid are large porcelain or stoneware vessels set in tanks, in which water is kept boiling by injected steam. They are fitted with hoods for carrying off the fumes to a condensing arrangement. Platinum vessels are also in use, each being heated over its own fire.

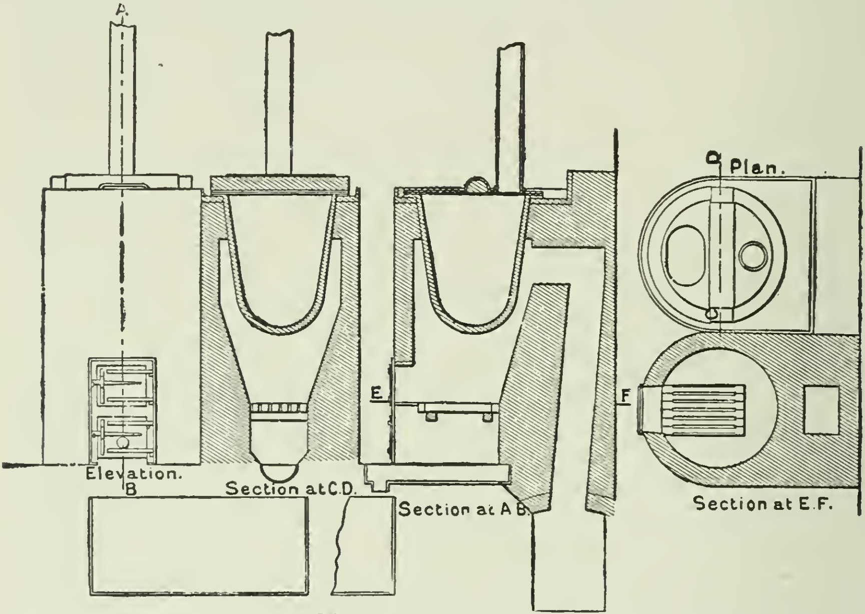

Fig. 151.—Parting Pans.

The granulations are heated for about four or five hours with 1$\frac{1}{2}$ times their weight of nitric acid (sp. gr. 1·2), when most of the silver is dissolved. The solution is then allowed to settle, and when clear is siphoned off into other stoneware vessels, where it is diluted with water to prevent the silver nitrate from crystallizing.

The gold remaining in the boilers is then again heated with fresh strong acid (sp. gr. 1·4) for two or three hours, and sometimes again with fresh acid for one or two hours, the solution being siphoned off as before.

The gold, which is in a pulverulent condition, is now well washed in stoneware dishes with boiling water, dried at a red heat in plumbago "annealing" pots, then melted and cast into ingots of 200 or 400 ozs. Fineness, 997 to 998·5.

The silver is obtained from the silver nitrate by precipitating it as silver chloride by a solution of common salt carefully added, vigorous agitation being kept up with wooden paddles. When the precipitate has subsided the supernatant liquor is drawn off, and the precipitate repeatedly washed with boiling water.

It is then transferred to lead-lined tanks, where it is reduced to metallic silver by means of zinc and water acidified with sulphuric acid.

When reduction is complete, a little sulphuric acid is added to dissolve any zinc which may be present. The reduced silver is then washed repeatedly with boiling water, pressed in a hydraulic press, melted, and cast into ingots of about 1,000 ozs. each, which should be about 998 fine.

Parting by Sulphuric Acid.—This process has entirely superseded the nitric acid method, as it is much less expensive, owing to the low price of sulphuric acid and the use of cast-iron pans. It is based on the solubility of silver in sulphuric acid.

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O$$

The appliances required are :—

A. Tub for granulating the bullion, as already described.

B. The pans (Fig. 151). These are of white cast iron, containing from 2 to 4 per cent. phosphorus, with hemispherical bottoms in Europe, but flat bottoms in America. In capacity they range from 2,000 to 12,000 ozs. of bullion.

The cover of the pan is of cast iron coated with thick sheet lead. There are two openings in the cover, each having double vertical projecting rims, so as to form a water joint. One is for introducing the granulated alloy, the acid, and an iron spatula for stirring, and for observing the progress of the operation. To the other a pipe is fitted for the escape of the vapours which pass through it to a leaden flue, where some sulphuric acid is condensed, and thence to the chimney stack. In this flue any silver sulphate which may be carried over mechanically is also collected. Each pot is set in brickwork over its own fire.

C. Several settling pans of copper.

D. A series of rectangular cast-iron tanks lined with lead, in which the silver is precipitated on copper plates.

E. Others in which the liquids from these are allowed to settle.

F. Cast-iron pans similar to but smaller than the boiling pans, in which the gold residues are boiled with fresh acid. Platinum pans are also in use, but are not necessary.

G. Hydraulic press for compressing the spongy precipitated silver.

H. Cast-iron rectangular evaporating tanks, lined with lead, for the evaporation of the copper sulphate solutions. Each of these is set in brickwork and is heated by a fire below it.

The Process.—The metals to be operated on may be divided into three classes.

I. Silver containing small quantities of gold, and almost free from the baser metals.

II. Gold containing small quantities of silver and almost free from the baser metals.

III. Impure gold and silver bullion, generally containing excess of copper.

Bullion of the first two classes can by proper admixture be treated, so that fine silver and fine gold can be obtained in one process. A small proportion of copper will not affect the result.

Bullion of Class III., which may contain, besides gold and silver, Pb, Sn, Cu, Sb, As, Zn, Fe, etc., requires to be treated twice for its gold contents, but most of the silver can be extracted during the first treatment. In ordinary practice, bullion of the 1st and 2nd class—viz., silver containing a little gold and gold containing a little silver—are mixed in such proportions that an alloy of 2½ or 3 parts of silver to 1 part of gold will be obtained. It is melted and granulated, as already described.

In America, however, the metal is not granulated, but is simply cast in the form of flat plates about ¾ inch thick.

The granulated metal, after draining a little, is placed in one of the boilers and boiled for two or three hours with from 2 to 2½ times its weight of sulphuric acid of not less than 1·820 specific gravity, with frequent stirring with an iron stirrer. At the end of, say, three hours the gold will be left in a spongy state, and the silver will be in solution.

The whole is now allowed to cool and settle. A little cold acid is sometimes added to the hot solution, this causes the formation of some crystals of silver sulphate, which, on settling, carry down with them any fine particles of gold that may be in suspension. As soon as the solution is clear it is baled out into the settling pans, and transferred from them to the precipitating vats, which already contain hot water, or hot mother liquor from a previous precipitation, and also copper plates or copper scrap.

The spongy gold is now baled into an enamelled iron basin, and the greater part of the copper sulphate and part of the silver sulphate adhering to it washed away with hot water and sulphuric acid.

After several washings with boiling water, and when the liquors are no longer very blue, the gold is introduced into one of the small iron boilers, with enough sulphuric acid to remove the silver sulphate, and boiled for 1½ hours or an hour.

The gold is then removed as before, washed in the same manner, and if the amount of base metals is large introduced into another small boiler and again boiled with more acid.

The gold is then washed repeatedly with boiling distilled water. When the washings are no longer acid, the gold is carefully drained and put into plumbago "annealing" crucibles.

These are very gently brought to a dull red heat and then removed from the fire. The gold, now ready for melting, must be melted in a clay crucible, and no reducing agent must be employed, or any lead, tin, etc., present, would be immediately reduced, otherwise they would float on the top as impure "litharge." Sometimes nitre and potassium bisulphate are used as fluxes. The gold is cast into ingots, which should be from 997 to 999 fine.

In casting gold ingots the mould should be warm, well oiled or smoked with pine wood, and the crucible moved backwards and forwards during pouring.

A little oil should be poured upon the gold, as soon as it is cast, and the mould covered with an iron plate. Immediately the gold has solidified the ingot should be turned out and brushed well all over with a cocoa-fibre brush, and then plunged into cold water.

The solution of sulphates in the precipitation tanks, containing copper plates or strips, is kept well boiled by injecting steam, and stirred all the time of the precipitation, to prevent silver sulphate from settling in the corners or under the precipitated silver. When the liquid no longer shows the presence of silver, on testing with salt, it is allowed to settle, and is then siphoned off into settling tanks.

The precipitated silver is then shovelled into a shallow copper pan with perforated bottom, thoroughly washed with boiling water until free from copper sulphate, allowed to drain, then pressed in a hydraulic press.

After pressing, it is melted in a plumbago crucible with a little nitre, to remove any copper or lead, etc., that may be present, and cast into ingots. The silver should be 997 to 998 fine.

Treatment of Bullion of Class III.—Impure gold and silver bullion generally containing excess of copper. After removal, if necessary, of any excess of copper it is granulated, and the granules are boiled with sulphuric acid, as described above. When all action has ceased, and the contents of the pan have cooled, the whole is baled out, transferred to a tank containing hot copper mother liquor or water, and boiled by steam injection. After settlement, the clear liquor is siphoned off into a precipitating tank, containing copper plates, and the silver precipitated in the usual manner.

The residue in the first tank is boiled once or twice with weak mother liquors when most of the silver sulphate is removed. The residue now consists of gold, some silver sulphate, and sulphates of lead, copper, etc. Copper plates are thrown in, and all the silver remaining as sulphate is reduced.

The residue is now washed thoroughly, dried and melted in a clay crucible to avoid reduction of base metals, and cast in a conical mould. An alloy of gold and silver will be found at the bottom of the mould, and litharge containing the base metals at the top. The alloy is assayed and re-parted.

If the bullion to be treated consists of good " doré " silver, containing only a little gold, and there is no refinable gold to alloy with it, the best plan is to alloy it with copper to 900; granulate or cast into thin plates, and dissolve as above, but with three times its weight of acid.

When dissolved, if allowed to settle for 12 hours, the anhydrous copper sulphate will carry down with it the fine particles of gold; the supernatant liquor can then be carefully baled off into the copper settling vessels, and at once decanted and precipitated in the precipitating tanks. The bottoms of gold and sulphates, etc., are then removed and boiled up in a tank with weak copper liquors, or water, and treated as already described under " impure bullion," by which means the gold contents become condensed into a much smaller proportion of silver. The resulting alloy is re-parted.

Treatment of the Copper Liquors.—When the liquors from the precipitation have been allowed to settle, they are evaporated in lead lined tanks until the specific gravity is 1·38. The solution is then transferred to other tanks, in which the copper sulphate crystallizes.

The mother liquor is again concentrated by evaporation and again crystallized. These operations are repeated until the whole of the copper is recovered as sulphate. The crude copper sulphate is purified by re-solution and recrystallization. The acid mother liquors are made use of as already described, or are concentrated and used with fresh acid in the dissolving pans. The mother liquors are now frequently electro-deposited and the acid regenerated.

In Fig. 152 is shown a plan of the gold and silver room for parting bullion by sulphuric acid, at the Imperial Mint, Osaka, Japan, before the introduction of electrolytic processes there.

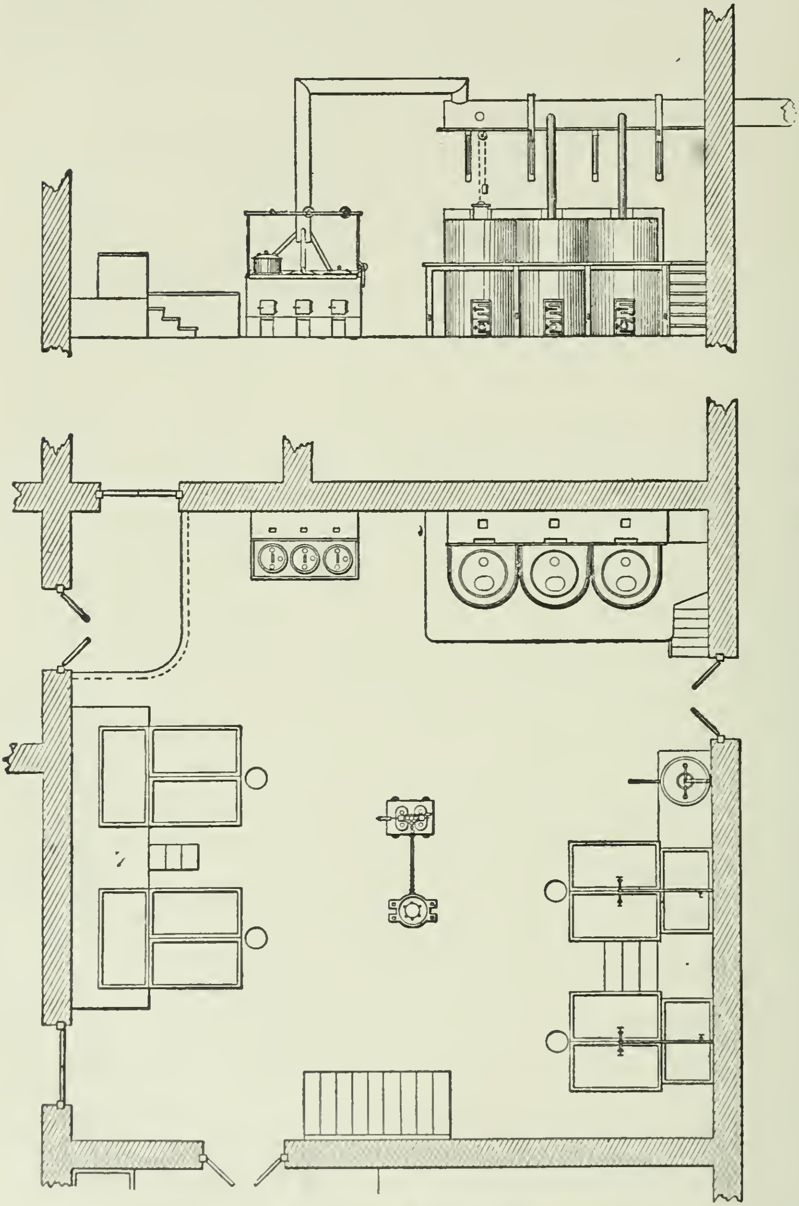

Fig. 152.—Gold and Silver Refinery (Imperial Mint, Osaka, Japan).

Gutzkow's Process.[*]—The following modification of the sulphuric acid parting process has been introduced by Gutzkow for the treatment of parting bullion, especially when containing much copper. It differs from the process as usually practised in the following points :—

1. The use of a large excess of sulphuric acid, thus for ordinary doré silver four times its weight of acid, and for bullion containing 20 per cent. of copper six times its weight is used, while when more impurities are present even larger amounts are employed. These large excesses of acid keep the copper in solution, and prevent it from interfering with the parting.

2. The boiling takes place in a cast-iron pot, 4 feet in diameter and 3 feet deep, with a flat bottom, in the centre of which is a basin-shaped pocket for the collection of the gold. The bullion is in the form of cast plates.

During the operation, after most of the silver has been dissolved, mother liquor from a previous boiling is added from time to time until the remainder is in solution.

3. The silver sulphate formed is crystallized, and reduced with charcoal, as follows :—

The solution after settlement is siphoned off into a large shallow cast-iron vessel, about 1 foot deep, standing in a tank which can be filled with water for cooling the charge. Steam is then passed into the solution, by which it is both diluted and warmed, the heating being necessary to prevent the silver sulphate from crystallizing. As soon as the dilution has proceeded sufficiently far to ensure the crystallization of the yellow monosulphate of silver, instead of the white bisulphate, the steam is shut off, the vat cooled with water, and left all night. The mother liquor is then pumped off, and the crystals are shovelled into a filtering box, provided with a false bottom. In this box they are washed with water to free them from acid, and copper and iron sulphates. The washings, which contain some silver sulphate, are run into a lead-lined vat, or through a filter box, containing precipitated copper, where the silver is precipitated.

The crystals of silver sulphate, after washing, are dried in an iron pan, then mixed with 5 per cent. of charcoal, and charged into a red-hot crucible. The charge is first heated to a low red heat, when the silver sulphate is reduced, CO_2 and SO_2 being evolved. The temperature is now raised to the melting point of silver. Nitre and borax are then added to toughen the metal, after which it is cast into bars.

4. The residue in the dissolving pan is ladled out, boiled with water to remove silver, copper, and iron sulphates, and afterwards stirred in a dish with hot water and decanted on to a filter cloth to wash away insoluble lead sulphate.

The gold is then melted and cast into a bar, which is usually brittle and requires refining. In the original Gutzkow process the crystals of silver sulphate were reduced by running over them in the filtering box a solution of ferrous sulphate, the reaction being as follows :—

$$2FeSO_4 + Ag_2SO_4 = Fe_2(SO_4)_3 + 2Ag.$$

Parting by Chlorine Gas, Miller's Process.—This process is especially suitable for removing small quantities of silver from gold bullion. It also eliminates lead, antimony, and other impurities, and thus removes the brittleness produced by them.

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[*] Rose, *Metallurgy of Gold*, p. 445, *et seq.*

If, however, a large amount of silver containing gold is available for parting gold bullion the sulphuric acid process is cheaper than the chlorine process.

On the other hand, where there is a scarcity of such silver, as in Australia, the chlorine process is the cheapest.

The bullion treated by it at the Melbourne Mint during 1910 contained gold about 919·0, silver about 41·0 per 1,000 parts; and at the Sydney Mint in 1910 gold 867·9, silver 88·8; the gold obtained at Melbourne assaying 995·0 and at Sydney 996·4. The process is based on the fact that gold has no affinity for chlorine at a red heat, but chlorine readily combines with the metals with which it is usually alloyed, forming chlorides.

Any silver present is converted into a fusible chloride, which floats on the surface of the molten gold, while the lead, antimony, etc., are converted into volatile chlorides, and are volatilized.

The process is carried on as follows:—

The crucibles are of white clay, 10½ by 5 inches, and are placed in the furnace in a "guard" pot of plumbago, the guard pot being afterwards used for melting the refined gold. The clay crucibles are covered with a lid, perforated with two holes, or with a notch in the edge, through which the clay pipes for introducing the chlorine are inserted. The bore of the pipes is ⅛ inch diameter. The furnaces are 12 inches diameter and 21 inches deep.

The generators are three-necked cylindrical stoneware vessels, sometimes with an external flange round the middle to support them in a steam jacket, or they are simply set in an iron water bath. The openings in the necks serve respectively for charging in the manganese dioxide and acid, the insertion of the pressure tube, and of the tube through which the chlorine is emitted. The pressure tube which reaches to the bottom of the vessel is about 15 feet high, and is bent over at the top, so that when the evolution of the chlorine is stopped it can deliver the liquid from the generators into a receiving vessel, placed on a shelf above. In some cases a branch tube for the supply of acid enters the pressure tube a short distance above the opening into the generators, both tubes then being suitably fitted with stopcocks. The tubes are of stout combustion tubing. The bottom of the generator is covered by 4 inches of quartz pebbles, upon which rich manganese ore, broken to ¼-inch to ½-inch size, is placed.

Chlorine is generated by adding hydrochloric acid (sp. gr. 1·16) as required, and heating the generator by a steam or water bath. The arrangement of the plant at the Melbourne Mint without the generator is shown in Fig. 153. As the process is carried on there on a large scale the earthenware generators have been replaced by an Edwards' generator * of wrought-iron lined with lead.

The clay pot with its guard pot is placed in the furnace charged with 2 or 3 ozs. of borax and heated to redness.

The ingots of gold, amounting to 650 to 720 ozs., are then introduced, and when molten the clay pipe previously heated, and the chlorine having been turned on, is gradually pushed to the bottom of the pot. The flow of chlorine is adjusted, so that it is completely absorbed by combining with

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* For a description of this generator, see T. K. Rose, *op. cit.*, p. 461.

the silver and the base metals, no bubbling taking place. Towards the end of the operation the supply of chlorine is reduced to avoid spurting, and when the " flame " has a dark brown fringe, and gives a characteristic stain on a piece of clean pipe stem being placed in it, the gas is shut off. The clay pot is then removed from the fire, the gold allowed to solidify, and the still molten chloride poured into a mould. The pot is then broken, and the gold placed at once in the guard pot, remelted, and cast into two flat ingots.

The chlorides contain from 5 to 10 per cent. gold. This is separated by melting in plumbago crucibles, and sprinkling sodium bicarbonate repeatedly on the surface. Some silver is reduced, and the globules in settling to the bottom carry down with them all the gold except traces. The crucible is then removed from the furnace, the reduced metal allowed to solidify, and the fused chlorides are cast into slabs, 12 by 10 by 2 inches.

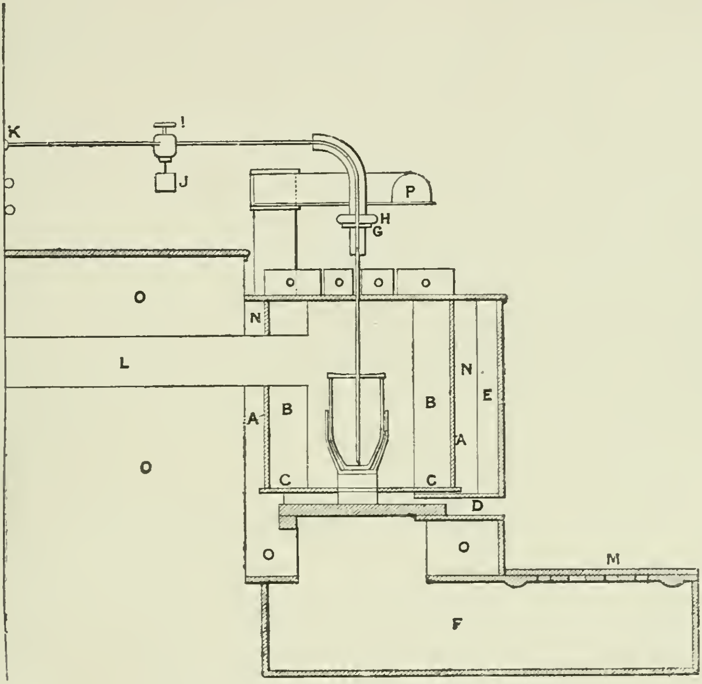

Fig. 153 —Parting by Chlorine, Melbourne Mint.*

The button of reduced metal contains 40 to 50 per cent. of gold.

The slabs of chloride are placed in flannel bags and boiled in water for four or five days to remove copper. They are then arranged alternately with iron plates in a tank of water, containing some liquor from a previous operation. Steam is injected and the reduction is complete in two or three days.

The reduced silver is washed with boiling water, melted with a small quantity of nitre, and cast into ingots. The silver should be 990 fine.

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* Rose, *Gold*, p. 453.

Parting by Chlorine at the Royal Mint, Ottawa.—At the Royal Mint, Ottawa, the gold received varied so much in its content of silver and base metals, sometimes as much as 15 per cent. Pb and 10 per cent. Cu being present, that considerable difficulties were met with in the electrolytic refining process. Miller's process has hence been adopted with some modifications for the preliminary treatment of this rough gold.

Details of the practice followed are given by Mr. Pearson in a paper in the *Bulletin* of the Canadian Mining Institute, July, 1915, of which the following is an abstract:—

The chlorine used is supplied from steel cylinders, each of which contains 100 lbs. of liquid chlorine.

Two cylinders are used, connected by a main pipe to two ½-inch lead pipes, and arranged so that the chlorine from either cylinder can be supplied to either of these pipes. Glass stop-cocks for regulating the flow of gas are attached by heavy rubber tubing to the ends of the lead pipes immediately above the furnaces.

The pipes are connected by branch pipes with a lead vessel with three necks similar to a Woulfe's bottle. A lead pipe, connected with a glass tube which carries a lead bulb, rises from the third neck. Sufficient water is placed in the lead vessel to give a pressure column 11 feet 8 inches in height, which is equivalent to about 5 lbs. per square inch. If the pressure should exceed this, the water is forced up into the lead bulb and the gas escapes outside the building.

The furnaces are fire-clay cylinders enclosed in sheet iron, their internal dimensions being 15 inches deep and 8½ inches diameter. Crude oil at a pressure of 40 to 50 lbs. per square inch with air at 2 lbs. per square inch is used as fuel.

Special arrangements are provided for the condensation and collection of the volatile matter from the furnaces.

The furnace flues are connected with a condensing chamber, 20 feet long, 5 feet wide, and 4 feet high. From this the gases pass to another chamber, 20 feet long, 3 feet 6 inches wide, and 3 feet high, built at right angles to the first. From this second chamber the flue leads to the bottom of a tower, 20 feet high and 2 feet 6 inches diameter, at the top of which is a water spray. Any material washed out of the gases by the water spray is collected in an earthenware tank at the bottom of the tower. The tower is connected with a 12-inch earthenware exhaust fan.

The crucibles are the usual white-clay " chlorine " pots, placed in plumbago guard pots, and the passing in of the chlorine and the separation of gold from the silver chloride are carried out as in the Melbourne Mint.

The time needed for chlorination depends on the amount of impurities in the bullion. An ingot of 500 ozs. containing 140 ozs. base metal, chiefly lead, and 80 ozs. silver, required seven hours.

The treatment of the silver chloride after the gold has been removed from it is interesting.

The cakes of chloride are broken up into pieces about ½ inch square, folded in flannel bags to form a parcel about 18 inches long, 16 inches wide, and 2 inches thick. Each of these is placed in a cane basket, and the baskets are piled on top of one another in a tank of water heated by steam. The tank is divided into two compartments, between which there is free circulation of the water. The copper chloride is dissolved out from the silver chloride and the copper is precipitated by scrap iron placed in the second compartment of the tank.

The silver chloride, after being well washed, is reduced to metallic silver by iron plates in the usual way in water acidulated with hydrochloric acid.

The average fineness of the silver obtained is 995 per 1,000.

Modification of Miller's Process, Treatment of Gold Bullion with Chlorine Gas and Air.*—This process is a combination of Sir T. K. Rose's method for toughening gold bullion by means of air or oxygen gas with Miller's chlorine process. In bullion containing only gold and silver the final stages of Miller's process occupy only a short time, whereas with bullion which contains, besides gold and silver, varying quantities of certain base metals such as lead, antimony, etc., the final stages of the refining process take a considerable time, and it is in these stages that the major portion of the losses of gold occurs. In this new process the last traces of base metals are removed while there is still a considerable quantity of silver present in the bullion, and it is found to be an advantage to mix the bullion located with the most silvery bullion available.

The process is carried out as follows :—Two clay pipe stems are introduced into the molten metal. One is connected to an air compressor delivering air at a pressure of 6 or 7 lbs. per square inch, and the other to the chlorine generator. At the beginning of the operation the maximum amount of air is used and a very slow stream of chlorine. As the operation progresses the volume of air used is diminished and that of the chlorine is increased, until finally the air pipe is removed and chlorine alone is used. The process was introduced by Mr. R. R. Kahan at the Royal Mint, Perth, Western Australia, where it is found to diminish considerably the losses in parting; also that the chloride slags do not contain so much free gold as in the case when chlorine only is used.

PARTING AND REFINING BY ELECTROLYSIS.

The Moebius Electrolytic Process.—This process is in use for parting doré silver containing only small amounts of gold, 1·0 to 50 parts, or somewhat more, per thousand, and not more than about 10 per cent. of base metals.

The anodes of the doré silver are 18 inches long, 10 inches wide, and about ½ inch thick. They are supported by hooks from a rod connected at one end with the positive conductor, the other end being insulated from the negative conductor, and are enclosed in linen or cotton bags to catch the gold and insoluble impurities.

The cathodes are thin rolled plates of pure silver, which are soldered at their upper edges to a copper bar. The copper bar rests, at one end, directly on the negative conductor, and at the other end on an insulator on the positive conductor. They are slightly oiled to prevent adhesion of the deposited metal.

The cathodes are continually scraped on both sides by wooden scrapers attached to a frame, carried on wheels, which is moved backwards and forwards on the edges of each compartment of the vats. By this means the surfaces of the cathodes are kept free from loose crystals of silver.

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* R. R. Kahan, *Trans. Inst. Min. and Met.*, 1919, p. 35.

The electrolyte is a weak solution of silver nitrate, 0·5 to 1·0 per cent., acidulated with nitric acid, about 1·0 per cent., fresh acid being added from time to time to prevent the deposition of copper.

The vats are of wood, coated on the inside with asphalt or graphite paint Each vat is divided transversely into several, usually seven, compartments, in each of which are suspended three series of anodes and four series of cathodes. A deep tray, with perforated bottom covered with canvas, is placed at the bottom of each compartment to receive the silver scraped from the cathodes.

The current should have an E.M.F. of about 1·5 volts per compartment

The current density is 30 to 20 ampères per square foot, and as the electrolyte becomes enriched in copper the lower density is employed, fresh nitric acid being added. When the copper in the bath reaches 5 per cent., part of the liquid is withdrawn, and replaced by fresh solution of silver nitrate, otherwise copper will be deposited on the cathodes.

In operating the process, the silver is deposited on the cathodes, scraped off, and collected in the tray, as described above. The gold, lead, platinum metals, and other impurities remain in the bags enclosing the anodes.

Each day the whole apparatus is lifted out of the vats by means of a frame, to which all is attached, including the collecting tray.

The deposited silver is removed, well washed, melted, and cast into ingots, which should be 999·0 to 999·5 fine.

The slime in the bags is removed once or twice a week, treated with sulphuric acid, well washed, melted, and the gold refined electrolytically.

In a later form of Moebius apparatus the silver is deposited on an endless band of silver, travelling over rollers, with arrangements for brushing off the deposited silver upon a travelling belt, by which it is delivered outside the vat. The anodes are laid above it in shallow troughs with bottoms of cloth, or porous clay plates.

The Moebius process is also in use for the treatment of the argentiferous and auriferous copper obtained by melting the mud from the electrolytic refining vats at Lithgow, New South Wales.*

The mud from the tanks is sifted, washed, heated to a dull red heat, and boiled with concentrated sulphuric acid. The residue is then washed, dried, and fused with sodium carbonate in a small cupel furnace to gold bullion, which usually assays about 12 to 16 per cent. Au, and 82 to 86 per cent. Ag. The bullion is parted electrolytically in an electrolyte of silver nitrate solution, a silver plate forming the cathode.

The gold is caught as a mud in calico bags, and after being heated with nitric acid, is fused, giving a fineness usually from 900 to 998. The silver is removed from the cathodes, by moving wooden arms, as fast as it is deposited. The crystals are finally collected and fused, the fineness being not less than 996 per thousand.

The United States Mint Silver Nitrate Process.—A modification of this process was in operation at the Royal Mint, Ottawa, in 1913 for the treatment of bullion containing larger proportions of gold than doré silver, but less than 800 parts Au per thousand.

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* *Journ. Soc. Chem. Ind.*, 1914, p. 202. Abstract of paper by G. H. Blakemore in *Trans. Australian Inst. Min. Engineers*, 1911, p. 36.

"Gold bars * over 900 fine are passed at once to the gold cells (see p. 371). Gold bars less than 900 fine are alloyed with silver, or, if possible, made up of mixtures of gold deposits of varying fineness, to form an alloy of 40 per cent. gold, 55 per cent. silver, and 5 per cent. base metal. From experiment 40 per cent. gold seems to be the maximum amount of gold possible for parting. This mixture is melted in plumbago crucibles capable of holding about 3,000 ozs. The metal is well stirred before pouring, and is cast into bars, each 15 inches long, 3 inches wide, and $\frac{3}{8}$ inch thick. These bars constitute the anodes for the silver cells, and weigh about 100 ozs. each.

"The electrolyte, which is a solution of silver nitrate containing 3 to 4 per cent. silver and about 2 per cent. free nitric acid, is contained in an earthenware tank holding about 400 litres, of the following dimensions, 4 feet long, 2 feet wide, and 2 feet deep. On the sides of the tank, at the top, are placed strips of hard rubber, with grooves cut out, running the length of the tank. In these grooves are placed $\frac{3}{8}$-inch steel rods covered with hard rubber tubes, the ends of which are plugged with the same material. The rods have a strip of silver on top $\frac{5}{8}$ inch wide and $\frac{1}{20}$ inch thick, shaped to fit the rod. The anodes and cathodes are suspended from the strip, which carries the current.

"The cathodes are strips of fine silver, 21 inches long, 3 inches wide, and $\frac{16}{1000}$ inch thick, annealed to within 3 or 4 inches of the top and bent over to fit the rods.

"The anodes are suspended by gold hooks slipped through the hole in the end, and are enclosed in cotton bags, which are tied at the top round the hook with string. The whole of the anode is immersed in the electrolyte.

"Alongside the grooved hard rubber, above mentioned, is a copper rod, $\frac{3}{4}$ inch square, running the length of the tank, to which the silver strips which carry the current are attached by means of brass screws and washers.

"The current is divided by splitting the leads from the dynamo and connecting to the copper rod in two places, so that the distribution through the cell is more even.

"In the middle of the tank is a glass stirrer or propeller, revolving at about 350 revolutions a minute, and causing an upward current in the liquid. The propeller is driven by a $\frac{1}{2}$ H.P. motor. If the electrolyte is not stirred the deposit is uneven and short circuiting takes place owing to the deposit 'treeing.'

"The hard rubber-covered steel rods are of two sizes, the short ones 2 feet 3 inches long, and the long ones 4 feet 10 inches long. The tanks are placed close together, and the long rods go across two tanks, and the short ones one tank. Two or more tanks are connected up in series, the current entering through the lines of anodes, which are in parallel, passing to the lines of cathodes, also in parallel, and by means of the silver strips on top of the long rods to the anodes in the next cell, and so on through the whole series.

"In each tank there are nine rows of anodes, five in each row, and nine rows of cathodes, five in each row, except in the middle row, where there are only four anodes and four cathodes, to allow room for the stirrer. The rows of anodes and cathodes are separated by a distance of $2\frac{1}{2}$ inches. The

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* Rose, *Metallurgy of Gold*, p. 471. Private communication to Sir T. K. Rose from Mr. A. L. Entwistle.

weight of the 44 anodes in the tank is about 4,400 ozs., consisting of gold 1,760 ozs., silver and base metal about 2,640 ozs. There are ten tanks in use, set up in series, standing upon strong wooden tables.

"The current used is 350 to 400 ampères at 8 to 9 volts, therefore each cell requires about 0·8 volt. The current density is about 25 to 29 ampères to the square foot. The silver dissolves from the anodes and is deposited upon the cathodes, the base metals being converted into nitrates and going into solution. The deposit of silver is brilliantly crystalline and coherent. The cathodes are taken out once in twelve hours and scraped with a silver scraper into a large porcelain filter, which is pulled around on a truck. When filled the filter is hoisted up on to a wooden platform by electric power, and the metal is washed free from silver nitrate, copper nitrate, etc., with hot water, and dried in a copper pan. It is then ready for melting and casting into ingots, the fineness being 999·5 or over.

"A little silver is detached from the cathodes in lifting out, and falls to the bottom of the tanks. The anodes are enclosed in cotton bags to prevent any small particles of gold from being carried over to the cathodes mechanically; also in case the anode should break, which sometimes happens, the bag prevents the broken pieces from falling to the bottom of the tank.

"When separation is complete the gold is left in the original shape of the anode, and is of a dark brown colour, which is easily broken with the fingers and is quite spongy. This is packed into a porcelain filter and washed free from silver nitrate with hot water, allowed to drain, melted without drying, and cast into gold anode plates for further treatment by the gold chloride process. The fineness of the plates is 940 in gold, and the remainder silver, with a little copper, lead, etc., and any platinum that may have been present in the original gold.

"If the passage of the electric current is continued after the anode reaches 940 fine in gold, the silver almost ceases to dissolve, and bubbles of gas are evolved at the anode. If the deposit becomes at all soft and mushy the electrolyte requires more silver nitrate, and if it does not adhere to the cathode more nitric acid is required. Racks placed above the tanks are lowered at night, and the cathodes taken out and hung on them to prevent the silver from dissolving and taking up the free acid. The refinery does not work at night.

"The anodes are taken out just before the bubbles of gas begin to be evolved, which occurs after about 95 hours; the men handling the cells become very expert in judging when the process is finished.

"The cathodes are used until they become too heavy, when they are melted with the crystalline silver and cast into ingots. The cotton bags are used about twice. The electrolyte is used until it becomes foul with impurities. When the specific gravity reaches about 1·320, about half of the solution is drawn off and fresh silver nitrate and water added. The foul solution, which contains from 3 to 6 per cent. silver and a large amount of copper, etc., is run into another tank and nearly all the silver is electro-deposited, iron anodes and silver cathodes being used. There is still a little silver left in solution, which is precipitated with salt solution, and the copper is then electro-deposited or recovered with scrap iron, if of sufficient value.

"All the washings from the fine silver, etc., are run into a large tank and precipitated with salt solution, and the silver chloride reduced to grey silver with iron plates and a little acid, washed, dried, and melted.

" The wash-water from the grey silver is run into a wooden tank containing iron plates and allowed to stand for several days before being run down the drain. This tank is cleaned out once a year, and the mud dried and melted. The resultant metal is found to contain about 1 per cent. silver and the rest chiefly copper.

" The disadvantage of the process is the length of time for treatment. The average gold received assays between 750 and 800 in fineness. Quite an appreciable amount of gold as received contains 30 per cent. or more of base metal. This material cannot be treated by the silver nitrate process, except a little at a time, and it causes the electrolyte in the silver cells to become foul very quickly. It would be better to treat it by the chlorine process (especially if it is preceded by treatment with oxygen, see p. 356). The chlorine process was to be used instead of the silver nitrate process after April, 1915."

Wohlwill Process, Electrolysis in Gold Chloride Solution.—Practice at the Ottawa Mint :—*

" Gold deposits of 900 fine and over, and the dark brown residue containing 94 per cent. gold from the silver cells are melted in oil furnaces, and cast into open iron moulds of the following inside dimensions :—6½ inches long, 3 inches wide, and ½ inch thick at the top, tapering to ¼ inch at the bottom. At the top of the mould there is a pin which leaves a hole in the plate produced. The anode is ¼ inch thicker at the top than the bottom, because the metal dissolves quicker at the top than the bottom, and so the whole anode is finished at the same time ; the anodes weigh about 90 to 100 ozs. each. The electrolyte contains about 50 grammes per litre of gold and about 5 per cent. free hydrochloric acid, and is contained in a white porcelain tank 16½ inches long, 11⅝ inches wide, and 11 inches deep. The cathodes consist of strips of fine gold 2½ inches wide, 10 inches long, and $\frac{15}{1000}$ inch thick, annealed to within 2 inches of the top, and are bent over to fit the rod from which they are suspended.

" The supporting rods are made of ⅜-inch steel, and are covered with hard rubber tubes, the ends of which are plugged with hard rubber. The current is carried by strips of gold or of fine silver $\frac{1}{16}$ inch thick, which run along the top of the rubber-covered rods. The cells are connected up in series. The anodes are suspended by a gold or silver hook slipped through the hole in the end and immersed almost up to the hook, in the electrolyte. The cells are kept at 60° C. by a sand-bath placed on an electric heater. The cells are placed in a lead-lined wooden tank, which is enclosed with glass sliding panels and covered with a hood, which has an outlet into the air through the roof, so that the acid fumes do not get into the room.

" The current is divided by splitting the leads from the dynamo and connecting to the copper rod, at each end of the bank of cells, in two places, so that the distribution through the cells is as even as possible. In the centre of the cell a hard rubber propeller or stirrer revolves at about 350 revolutions a minute, so that it draws the liquid up. The current is divided between the eleven anodes, which are arranged in four rows, with a space in the middle to allow room for the stirrer. There are also eleven cathodes. The leads from the dynamo are connected to two copper rods above the cells, one positive, the other negative, running the whole length of the cells. There are eighteen cells set up in series, but six cells are generally out of use for cleaning purposes. The cleaning of a set of six cells is begun about twice a month. These six are cut out of the circuit and the other six put in, so that twelve cells are constantly running. The ten silver cells (see p. 370) supply just sufficient gold to keep the twelve gold cells running.

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* Rose, *Metallurgy of Gold*, p. 484. Private communication to Sir T. K. Rose from Mr. A. L. Entwistle.

" The current used is 150 ampères at 12 volts for the twelve cells, and the current density is about 100 ampères per square foot. (Reckoning both sides of the anode, it appears to work out at about 50 ampères per square foot.) An anode weighing about 70 ozs. is dissolved in about forty-two hours (nearly a week's work), when the residue or top is taken out and replaced by a new anode. When new cathodes are put in the cells the current is lowered to 50 to 100 ampères. If the current is kept up to 150 ampères, the first deposit is soft and mushy, and does not adhere to the cathode, but after two or three hours at the lower current it is quite hard, and then the current is put up to 150 ampères again. If the deposit subsequently becomes mushy and soft, the cell requires the addition of more gold chloride, and if chlorine is evolved at the anodes more hydrochloric acid is required. About a pint of gold chloride solution, containing 20 per cent. gold and 10 per cent. hydrochloric acid, is added to each cell every morning. The evaporation, due to heating, just allows a pint of chloride solution to be added to keep the electrolyte up to within 1 inch of the top of the cell.

" The cathodes are taken out when they are about 60 to 80 ozs. in weight, placed in a porcelain filter, washed free from gold chloride, etc., allowed to drain over night, and melted in plumbago crucibles and cast into iron moulds, the fineness being 999·3 to 999·5.

" The twelve gold cells produce about 4,000 ozs. per week of forty-four hours, but about 600 ozs. of this are cast into bars and rolled out to make new cathodes.

" The gold in the foul electrolyte and from washing slime, etc., is precipitated with sulphate of iron, allowed to settle, and the liquid siphoned off and run into an earthenware tank containing iron plates, which brings down the platinum and copper.

" The slimes from the cells are washed free from gold chloride with hot water and then placed in an earthenware tank, with iron plates at about a distance of 3 inches apart, and acidified with hydrochloric acid."

The silver, after treatment with hydrochloric acid and washing, is melted and cast into ingots, which contain about 60 to 70 per cent. gold.

The process, as compared with the sulphuric acid parting process, requires more care and intelligence in carrying it out, and the losses are liable to be greater on account of having gold in solution in the electrolyte. On the other hand, the gold obtained is purer, all the platinum metals are saved, and no nuisance is caused by acid fumes.

" The chief defect is the greater length of the time of treatment, so that if the loss of interest on the gold is taken into account a grave disadvantage is disclosed " (*Rose*).

The adoption of the Wohlwill process in the United States has increased the recovery of platinum and palladium.

SILVER.

Physical Properties.—Silver is the whitest of metals, and is capable of receiving a brilliant polish. It is harder than gold, but softer than copper.

Malleability and Ductility.—With the exception of gold, it exceeds all the other metals in these properties. It is said that it can be hammered into leaves only $\frac{1}{1000}$ of an inch thick, and a single grain can be drawn into 400 feet of wire.

Tenacity.—The tenacity of silver at 0° C. is about 18 tons per square inch (*Baudrimont*).

Specific Gravity.—The specific gravity of cast silver is 10·50, and after being struck in a coining press 10·57.

Action of Heat.—The melting point of silver is 962° C., and its boiling point 1,850° C. (*Moissan*). According to the Bureau of Standards at Washington, the melting point is 960·5.

When silver is melted in crucibles there is a slight volatilization if it is heated much above its melting point. Its volatility is much increased in the presence of Pb, Zn, As, and Sb, and to this the loss of silver in roasting furnaces, in which the temperature is never sufficiently high to volatilize the pure metal, is largely due.

When silver is melted in the air, it absorbs about twenty-two times its volume of oxygen, and this is given off with effervescence as the metal solidifies. When cast in an ingot mould, the upper surface of the ingot will be covered with protuberances, resembling miniature volcanoes, and particles of silver will be projected to some distance. This phenomenon is termed "spitting" or "sprouting"; it only occurs when the silver is comparatively pure, and is prevented by the presence of small quantities of copper or lead, or by stirring the metal under a cover of charcoal. "It is probable that the oxygen exists in the molten silver in the form of the oxide, Ag_2O, as this substance has been shown to be stable at very high temperatures, although it is instantly decomposed at a red heat" (*Rose*).

Electrical Conductivity.—The conductivity of silver for electricity is higher than that of any other metal.

Atomic Weight.—The atomic weight of silver is 107·88.

Chemical Properties.—Silver is not acted on, at ordinary temperatures, either in dry or moist air. The blackening of silver articles in the air of towns is due to the formation of a film of silver sulphide from the presence of traces of H_2S.

Alkalis or alkaline carbonates have no action on the metal, even when molten. Nitric acid dissolves it readily, and is the best solvent. It is soluble in boiling concentrated sulphuric acid, but not in dilute acid.

Hydrochloric acid acts on it very slowly and only superficially, forming an impervious coating of chloride.

It is not attacked by other acids, but chlorine, bromine, and iodine act on it with the formation of AgCl, AgBr, and AgI. It is also soluble in cyanide solutions when in fine particles.

Silver also dissolves in solutions of sodium hyposulphite as a double hyposulphite of silver and sodium.

When finely divided silver is heated with common salt silver chloride is formed.

Silver Oxides.—There are two oxides of silver, AgO and Ag_2O, but they are of little metallurgical importance.

Silver Sulphide, Ag_2S.—On the properties of the sulphide and chloride the most important processes for the extraction of silver depend. It is dark grey to black, and is found native as the mineral argentite. Silver has a strong affinity for sulphur, and readily combines with it.

Silver sulphide is practically non-volatile at high temperatures, and remains unaltered if air be excluded, but if air be admitted it is decomposed metallic silver and sulphur dioxide being formed.

It is insoluble in solutions of the alkalis, their carbonates, and chlorides, and in sodium thiosulphate (hyposulphite), but is soluble in solutions of potassium and sodium cyanides, and of double hyposulphite of sodium and copper (see p. 418). It is also soluble in strong nitric acid, sulphur being separated and silver nitrate formed, and is decomposed by strong sulphuric and hydrochloric acids.

Sulphide of silver is soluble in molten copper sulphide, lead sulphide, and other metallic sulphides forming argentiferous mattes, and on this property the extraction of the metal by matte smelting processes from copper and other ores depends. Metallic silver, silver chloride, and bromide also dissolve in mattes as sulphide.

In amalgamation processes mercury decomposes the sulphide, the resulting silver forming an amalgam with the excess of mercury present. The reduction of the silver is greatly increased when a solution of alum, ferrous sulphate, or cupric sulphate is added.

Sulphide of silver is completely reduced by iron at a red heat, but the iron must be in slight excess (*Karsten*); while copper and lead only effect partial reduction. When heated with an excess of nitre the whole of the silver is reduced, but with alkaline carbonates and cyanides the reduction is not complete. When heated in air, even at the lowest temperature at which a change takes place, it is reduced to metallic silver, no sulphate being formed.

If silver sulphide be fused with PbO or CuO, decomposition takes place, as follows :—

$$Ag_2S + 2CuO = 2Ag + 2Cu + SO_2.$$

If it be fused with Ag_2SO_4, metallic silver is produced—

$$Ag_2S + Ag_2SO_4 = 4Ag + 2SO_2.$$

For the changes which occur when silver sulphide is roasted with other sulphides and with sodium chloride, see pp 392 and 393).

Silver Chloride, AgCl.—Occurs native as the mineral kerargyrite. Silver chloride is largely produced in many metallurgical operations, such as chloridizing roasting, etc. It is also formed by the action of cupric, ferric, and mercuric chlorides on silver, thus—

$$2CuCl_2 + 2Ag = 2AgCl + Cu_2Cl_2.$$

It is readily soluble in hot solutions of sodium thiosulphate, ammonium, calcium, and magnesium chlorides, alkaline cyanides, and hot concentrated hydrochloric acid. Almost completely insoluble in water.

Other important reactions are given on pp. 386 and 393.

Silver chloride is completely reduced when fused with alkaline hydrates and carbonates, sodium carbonate being generally employed, thus—

$$4AgCl + 2Na_2CO_3 = 4Ag + 2CO_2 + 2O + 4NaCl.$$

Also, when fused with 1 part of charcoal to 2 parts of chloride, the silver is reduced.

In the wet way zinc and iron are the best reducing agents—

$$2AgCl + Zn = 2Ag + ZnCl_2.$$

Copper reduces it perfectly from ammoniacal solutions, and from strong sodium chloride solutions, but not satisfactorily from acid solutions. Mercury reduces it slowly, according to the equation—

$$2AgCl + 2Hg = 2Ag + Hg_2Cl_2.$$

The action of mercury is promoted by the presence of cupric sulphate, ferrous sulphate, and alum; also by the presence of iron.

Silver Sulphate, Ag_2SO_4.—Very largely produced in the operation of "parting" (p. 359). It is soluble in hot water, but the best solvent is sulphuric acid of specific gravity 1·25. In cold water it is only slightly soluble. The silver is completely precipitated from solutions of silver sulphate by Cu, Fe, Zn, Sn, and Pb. In solutions obtained in gold and silver parting by sulphuric acid, and in those of the Ziervogel process, copper is always used as the precipitant.

It is completely reduced by charcoal at a dull red heat as in the new Gutzkow process (p. 363), the reaction being—

$$Ag_2SO_4 + C = 2Ag + CO_2 + SO_2.$$

The crystals are also reduced in the old Gutzkow process by ferrous sulphate—

$$Ag_2SO_4 + 2FeSO_4 = 2Ag + Fe_2(SO_4)_3.$$

Silver sulphate is decomposed at a bright red heat into silver, oxygen, and sulphur dioxide.

Silver Bromide, AgBr.—Occurs native as the mineral bromite. It is soluble in most of the solvents of silver chloride, but generally to a less extent.

At the Utrecht Mint, sodium bromide is used instead of sodium chloride for the precipitation of silver in the volumetric process of assay.

Silver Iodide, AgI.—Occurs native in the mineral iodite. It is soluble in solutions of alkaline cyanides and hyposulphites, but only very slightly in solutions of alkaline chlorides.

Silver Cyanide.—The double cyanides of silver and potassium, $KAg(Cy)_2$, and of silver and sodium, are of great importance in the metallurgy of silver, since the introduction of the cyanide process for the extraction of silver from its ores. Silver is precipitated from their solutions by zinc, copper, aluminium, sodium sulphide, and by electricity.

Silver Bullion.—Silver bullion is the term applied to silver in the mass —*i.e.*, in ingots or bars—as distinct from coin or plate. When it contains gold it is called " doré " silver, and is then bought by gold and silver refiners. " Refined " silver is silver nearly pure and practically free from gold. It usually contains from 997·5 to 998·5, or occasionally 999·0 parts of silver in 1,000 parts, when it is said to be 997·5, 998·5, or 999·0 fine.

" Fine " silver is chemically pure silver.

In the London market the price is quoted per ounce Troy, in terms of standard silver (925 silver per 1,000). In New York the price quoted is for fine—that is, pure silver.

The impurities generally present are copper, lead, and sometimes zinc and bismuth.

Alloys of Silver of Industrial Importance—*Silver and Copper.*—Silver can be alloyed with copper in all proportions, but the alloys are not homogeneous throughout, excepting the eutectic.

The eutectic alloy (71·89 per cent. of silver), which has been termed Levol's alloy, is perfectly homogeneous whether slowly or rapidly cooled. It has been used for coinage purposes for circulation in the Dutch Indies. Bars or ingots containing more or less silver than the eutectic are not of uniform composition, the former being richer at the centre than at the sides, and the latter richer at the sides than at the centre.* This fact is of great importance in the valuation of silver bullion, as it determines the manner in which the samples for assay should be taken. In such bullion it is necessary to take the assay piece by dipping out a small quantity of the molten metal with a charcoal dipper and granulating it by pouring it into water, and not by taking a cutting from the ingot. The granules should be well dried in a porcelain or other vessel on a hot plate, after they have been hammered flat, as they sometimes, but rarely, are hollow spheres and contain water.

In the Author's experience, "dips" are very rarely necessary in silver bullion when the fineness exceeds 975 and assay pieces can be cut from one of the bottom edges of an ingot, preferably at a point one-third distant from one of the ends.

The silver-copper alloys are in extensive use for coinage and silver wares of all kinds.

In England the alloy for plate,† other articles and for coins (prior to 1920) consists of 925 parts of silver and 75 parts of copper in 1,000 parts, and is known as " standard silver." In the United States, France, Germany, Italy, Japan, and other countries the alloy for the principal coins contains 900 parts of silver and 100 parts of copper, and is slightly harder than the English standard alloy. Alloys containing less silver are in use for the subsidiary coins in many countries; in France, Italy, Spain, Switzerland, etc., an alloy containing 835 parts of silver is employed, whilst in Sweden, Norway, and Denmark some denominations of the coins have only 400 parts of silver in 1,000 parts, and in England, since 1920, 500 parts.

" Standard silver " melts at 890° C.,‡ while the temperature of the metal in the crucible when ready for pouring is about 1,200° C., and the temperature of the stream during pouring is about 1,113° C.

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* See paper by S. W. Smith, *Trans. Inst. Min. and Met.*, 1926, vol. xxxv., p. 248.

† There is also another alloy for plate, containing 958·3 parts of silver, but it is seldom used, as it is less durable than " standard " silver.

‡ See E. A. Smith and H. urner, *J. Inst. Metals*, 1919, vol. xxii., p. 149.

The results of annealing tests on the rolled sheets of " standard silver " show that the lowest temperature at which softening begins to be perceptible is 230° C., the temperature at which softening is nearly complete in half-an-hour is 550° C., and in less than a minute 600° C. The avoidance of oxidation is necessary during annealing operations, and also during soldering, otherwise the copper oxide formed penetrates the metal, producing what is known in the silver trade as " fire-mark," which is difficult to remove by subsequent treatment.

The maximum tensile strength for " standard silver " as cast in a box mould is 11 tons per square inch, and for sand-cast metal 14 tons per square inch. The Brinell hardness of the metal as cast in a closed mould is 70 and as sand cast 67. The maximum Brinell hardness of the cold-worked metal is about 183, which corresponds to a tensile strength of 35 to 40 tons per square inch.

Dr. A. L. Norbury * has reported on the effect of quenching and tempering on the mechanical properties of " standard silver," and has shown that the alloy as ordinarily annealed contains a considerable amount of copper (in which some silver is dissolved) distributed in the form of small particles throughout the silver solid solution matrix. By suitable heating, for about half-an-hour at 770° C., and quenching, these copper particles may be dissolved and retained in supersaturated solid solution in the silver. The alloy when in the quenched condition is about 30 per cent. softer and 20 to 30 per cent. more ductile than it is when in the ordinary annealed condition.

On suitably tempering the quenched alloy, for example by heating for about half-an-hour at 300° C., its Brinell hardness number increases by about 300 per cent. and its tensile strength by about 50 per cent. ; at the same time its ductility falls by about 50 per cent. These effects are due to the decomposition of the supersaturated solid solution of copper in silver. The hardening on tempering is accompanied by a decrease in volume. The hardening obtainable by tempering is uniform and is consequently superior to the hardening obtainable by rolling, stamping, etc. It is possible to harden the quenched alloy by cold work and then further harden it by suitable tempering. The alloy is more resistant to oxidation and tarnishing when in the quenched and tempered conditions than it is in the annealed condition.

Silver and Zinc.—Alloys of silver and zinc have been investigated by Peligot with a view to their employment for coinage, as they do not tarnish. He found that those containing from 13 to 20 per cent. of zinc were fairly malleable, and an alloy of 80 per cent. of silver and 20 per cent. of zinc was not discoloured even by alkaline sulphides. Zinc has a strong affinity for silver, and will remove silver from lead at a temperature a little above its melting point ; on this property, the Parkes process for the desilverization of argentiferous lead depends.

Silver and Cadmium.—These alloys are softer, whiter, and more malleable and ductile than silver-copper alloys.

The alloy consisting of 925 parts of silver and 75 parts of cadmium has been shown by Sir T. Kirke Rose to be perfectly homogeneous, and it has been proposed by him to use it for standard trial plates at the Royal Mint.

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* *J. Inst. of Metals*, 1928, vol. xxxix. p. 145.

Silver and Lead.—Silver and lead, when melted together, unite in all proportions, but during solidification they segregate. Hence argentiferous lead when cast into pigs is not of uniform composition throughout. Satisfactory samples for assay cannot, therefore, be cut from the pigs, and it is necessary to remelt them and take dip samples (*Claudet*).

When silver-lead alloys are melted at a red heat, with free access of air, the lead is rapidly oxidized, the silver remaining unaltered. The process of cupellation is based on these properties.

Lead has a stronger affinity for silver than copper, so that when an alloy of copper and silver, with excess of lead, is heated to a temperature between the melting points of copper and lead, the lead will liquate, carrying the silver with it. The old liquation process now abandoned was based on this property.

Silver and Bismuth.—Silver alloys with bismuth in all proportions, and the latter metal may be separated from it by cupellation, but small amounts always remain in the silver, and produce brittleness.

Ingots of silver containing bismuth are not homogeneous; such ingots, even when of high fineness, hence must be assayed from "dips," and not from cuttings.*

Silver and Mercury.—Mercury dissolves silver forming amalgams, which are liquid or solid according to the percentage of silver they contain. The amalgam first formed on silver in contact with mercury does not readily dissolve in the surrounding mercury, but rather tends to hinder its further action; hence it is that, in the amalgamation of silver ores, grinding is so necessary to remove this layer and lay bare fresh surfaces of silver to the action of the mercury. It also follows that a siliceous gangue in ores facilitates and a clayey gangue retards amalgamation.

There seems to be only one definite amalgam, as when any liquid amalgam is squeezed through canvas or chamois leather the product remaining will always consist approximately of 30·4 per cent. of silver and 69·6 per cent. of mercury, which agrees with the formula Ag_2Hg_3, with 4·6 per cent. of free mercury.

Silver and Platinum.—See Platinum, p. 426.

Ores of Silver.—The most important ores, as sources of silver, and those which have the widest distribution, are the following:—

Native Silver.—It occurs in dendritic and wire-like forms, in laminæ, and sometimes in masses, and occasionally as a coating of native copper. It is often very pure, containing over 99 per cent. of silver. At Kongsberg (Norway) it has been found in very large masses, one of which weighed 697 kilos., and is still an important ore there. It is associated generally with other silver ores in Mexico, Chili, Peru, Broken Hill (N.S.W.), several localities in the United States, and at Cobalt (Canada.)

Argentite, Ag_2S.—Black in colour, soft and sectile. Very widely distributed: one of the commonest ores of silver in Nevada, Mexico, Broken Hill (N.S.W.), Peru, Cobalt (Canada), Japan, Saxony, and many other localities.

Kerargyrite, AgCl.—Wax-like in appearance and sectile, but rarely pure.

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* Gowland, *Journ. Chem. Soc.*, vol. li. (1887), p. 410.

Of wide distribution, and of considerable importance as a source of silver, especially in Mexico, Chili, and Peru, but much of it is in reality the chlorobromide (*Embolite*). It occurs in the upper oxidized parts of lodes.

Embolite, $x\text{AgCl} + y\text{AgBr}$.—Resembles kerargyrite in appearance. Chief localities—Chili, Mexico, Honduras, and Broken Hill (N.S.W.).

Stephanite, $5\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$, and *Pyrargyrite*, $3\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$.—Both are double sulphides of silver and antimony, are of common occurrence, often associated, and form important ores. The former is iron black in colour, and occurs in Mexico, Colorado, Saxony, and Bohemia. The latter is more or less red, sometimes dark grey, and is found in the above localities, also in Nevada, Idaho, Chili, Cobalt (Canada), and the Harz.

Proustite, $3\text{Ag}_2\text{S} + \text{As}_2\text{S}_3$.—Light red silver ore. It occurs in the same localities as pyrargyrite, and in Peru and Bolivia, but is less abundant.

Tetrahedrite or *Fahlerz* (grey copper ore).—The following formula, $4(\text{CuFeAg}_2\text{HgZn})\text{S} \, . \, (\text{SbAs})_2\text{S}_3$, has been assigned to it, but no two specimens agree in composition. It is often a valuable ore from its content of silver, which sometimes amounts to 31 per cent., being greatest in the non-arsenical varieties. It is of frequent occurrence, and is an important ore in Utah, Bolivia, Peru, Nevada, Colorado, Mexico, Cobalt, and Central Europe.

Polybasite, $9(\text{Ag}_2\text{Cu})\text{S}, (\text{SbAs}_2)\text{S}_3$.—Ag variable, 64 to 72 per cent.—Localities many, some of the chief being Idaho, Nevada, Mexico, Chili, Freiberg, and Przibram.

Dyscrasite, Ag_3Sb.—The proportions of Ag and Sb, however, vary greatly. Localities—Chili, Bohemia, Cobalt (Canada), and Broken Hill.

There are many other silver minerals, but they are not important to miners or metallurgists as sources of silver.

One of the richest localities for the production of silver that has been opened for many years is Cobalt in Canada. The ores are very variable in composition, and consist chiefly of native silver, argentite, dyscrasite, pyrargyrite, and tetrahedrite, associated with cobalt and nickel arsenides, sulphides, and arsenates. They are extraordinarily rich in silver; the richest lot in 1907 contained 7,402 ozs. per ton, and a considerable proportion of the others from 1,000 to 3,000 ozs., while the Co, Ni, and As averaged respectively 5·99, 3·66, and 27·12 per cent.

A very large amount of the world's production of silver is, however, not obtained from the true silver minerals, but from lead, copper, and zinc ores, in which it is an accidental constituent. The most important of these are galena and copper pyrites, which always contain silver, especially the former, in which from 1 oz. to 2,000 ozs. per ton may be present. Zinc blende is also frequently argentiferous, containing as much as 95 ozs. per ton at Laxey (Isle of Man). Iron pyrites, too, is occasionally but rarely argentiferous.

Extraction of Silver from its Ores.—*Processes.*—The chief processes employed for the extraction of silver from its ores may be classified as follows :—

Wet Processes.—(1) Amalgamation processes: (*a*) Amalgamation in low heaps with mercury with the aid of reagents; the Mexican or Patio process. (*b*) Pan amalgamation, without previous roasting; the Washoe process. (*c*) The Boss process; continuous system of pan amalgamation. (*d*) Pan amalgamation, with previous roasting.

(2) Cyaniding.

(3) The Augustin process, in which the Ag as AgCl is dissolved in brine.

(4) The Patera process, in which the Ag as AgCl is dissolved in solution of sodium thiosulphate (hyposulphite).

(5) The Kiss process, in which the leaching solution is calcium hyposulphite.

(6) The Ziervogel process, in which the Ag as sulphate is dissolved in hot water.

(7) The Russell process, in which the leaching solution contains double sodium copper hyposulphite.

At present the cyanide process has displaced or is displacing all the above, except in a few localities where special conditions prevail.

Dry Processes.—(8) Smelting with lead ores.

(9) Matte smelting. Smelting argentiferous ores containing small percentages of copper or non-cupriferous silver ores with pyritic ores containing copper.

(1) **Amalgamation Processes.**—In addition to the amalgamation processes mentioned, there are the Caso, Fondon, Kröhnke, Tina, and the Freiberg barrel processes, all of which have been successful in their day, and have produced large quantities of silver; but now they are for the most part obsolete, having been displaced by others more effective and economical, and need not be described.

(*a*) **The Patio Process.**—The Patio process has been in use in Mexico since the middle of the sixteenth century, and was still employed until recently, as it is especially suitable for dry barren districts, where both water and fuel are scarce, treatment difficult, and where comparatively low-grade siliceous ores, consisting of finely disseminated native silver, silver chloride, argentite, and stephanite occur. Pyrites and galena do not interfere, but zinc blende is said to diminish the yield. In recent years it has been displaced by the cyanide process at all important mines. It is everywhere falling into disuse, and rapidly becoming merely of historical interest. The chief materials required are only mercury, common salt, and "magistral" (an impure copper sulphate prepared from copper pyrites).

The ore is roughly broken by hand to the size of large walnuts, sorted, and then dry-crushed in Chilian mills to pass through a screen with $\frac{1}{4}$-inch holes.

It is then ground wet in arrastras (see p. 255) to fine mud, only sufficient water being used to yield mud of the proper consistence. Here any gold present in the ore is extracted by mercury. The mud is transferred to the amalgamation yard, allowed to dry, if necessary, until it is of the consistence of clay for brick-making. The yard is paved with flagstones with cemented joints.

It is then made into "tortas" or flat circular heaps about 12 to 18 inches in thickness, and containing about 100 tons of ore (dry weight). On the first day, about 5 to 6 per cent. of common salt is spread over the surface, and incorporated with the mud by driving six to twelve mules over every part of the heap.

On the second day, "magistral," or copper sulphate (about 6 to 9 lbs. of copper sulphate or its equivalent in magistral), is added and well trodden in by mules, as above.

Immediately after this mixing 6 to 8 lbs. of mercury for each pound of silver in the ore are added, by squeezing it through a canvas bag and scattering it in fine globules over the entire torta. The mud is again trodden to incorporate the mercury. After the second day samples are taken daily from every part of the heap, and tested by vanning, the appearance of the amalgam indicating the extent to which amalgamation has taken place, and whether the copper sulphate is deficient or in excess. If insufficient, more is added, and if in excess an addition of lime or copper precipitate is made. The heap is trodden by mules every day, or every other day, until the amalgamation is complete, which may require two, three, or four weeks. On the last day a fresh quantity of mercury, equal to about four times the weight of silver present is added, to render the dry amalgam fluid, and to assist in its collection. The material of the heap is then washed in a pair of large dolly-tubs, sometimes built of masonry with plug-holes in their sides, the agitators being driven by mule power. The tubs are first filled two-thirds with water, and the mud of the heap gradually charged in. The amalgam settles to the bottom, and the plugs are drawn successively from the first hole to the lowest, when the light mud flows away, and is led over riffles to catch sulphides and any amalgam which may have been carried over. The amalgam is collected in hide buckets, well washed, and the excess of mercury removed by squeezing through a canvas bag. The amalgam is made into balls, or beaten into cakes, and the mercury distilled from it as described on p. 394. The retorted amalgam is broken up while hot and melted, old quicksilver bottles with the necks cut off being used instead of crucibles. Two bottles are firmly bound together by a band of iron, and together hold 1,000 ozs. silver. The silver will range in fineness from 970 to 992, and usually contains 1·0 to 2·0 parts of gold per thousand. The yield of silver from 60 ozs. ore under favourable conditions at Zacatecas was 75 to 85 per cent. direct, and 8 to 10 per cent. from the concentrate, but it is generally much less. The silver lost in the tailings is tolerably constant, say about $2\frac{1}{2}$ to $3\frac{1}{2}$ ozs. per ton, and the loss of mercury averages about $1\frac{1}{2}$ ozs. for each ounce of silver in the ore.

The process was modified at Loreta in 1905, when the torta was made in the form of a long rectangle, 10 inches thick, and instead of mules, ploughs worked by electric motors moved up and down the heap, turning over every part of it, mules, however, being still employed for part of the work of salt-mixing.

The reactions are of a complicated character, and have not been exhaustively worked out, but the following equations represent fairly well the changes which occur, and doubtless several take place simultaneously:

(*a*) $2NaCl + CuSO_4 = CuCl_2 + Na_2SO_4.$
(*b*) $Ag_2S + CuCl_2 = 2AgCl + CuS.$
(*c*) $CuCl_2 + CuS = Cu_2Cl_2 + S.$
(*d*) $2CuCl_2 + 2Hg = Cu_2Cl_2 + Hg_2Cl_2.$
(*e*) $Ag_2S + Cu_2Cl_2 = 2Ag + CuCl_2 + CuS.$

The Cu_2Cl_2 is the chief reducing agent in the process, the action of $CuCl_2$ on Ag_2S (equation *b*) being very slow.

(*f*) $2AgCl + 2Hg = 2Ag + Hg_2Cl_2.$

This reaction, and also (*d*) can only partly take place, otherwise the loss of mercury due to the formation of Hg_2Cl_2 (calomel) would be very much greater than it is.

Any native silver is dissolved by the mercury.

The Pan Processes.—There are but few mills now running of the scores where pan amalgamation was formerly carried on, and it is extremely doubtful whether any new mills will be erected.

The processes, like the Patio process, have been and are being replaced by smelting and cyaniding.

(*b*) **Washoe Process.**—In this process the ores are usually wet-crushed, and are amalgamated without previous roasting. The process is so named from the district in which it was first introduced.

The ores for which it is suitable are those containing native silver, kerargyrite, embolite, and argentite, and free from arsenical and antimonial sulphides, tetrahedrite, galena, and blende, otherwise roasting with common salt is necessary before they can be amalgamated. The ore is broken in rock breakers to pass 1½-inch ring, and crushed by stamps with generally a double discharge (see p. 258) to pass a 40-mesh screen. The pulp is taken by launders to the amalgamation plant, where it is received in settling tanks, from which, after settling, it is shovelled on to the platform above the pans, and thence charged into the pans themselves.

The appliances of the amalgamation plant are as follows :—

1. Amalgamating pans.
2. Settlers, one for every two pans.
3. Clean-up pans.
4. Amalgam safe and strainer.
5. Mercury pump and elevator.
6. Amalgam retort.
7. Crucible furnace.
8. Riffle sluices, vanners, or tables for the spent pulp.

Amalgamating Pans.—There are many varieties of these pans, but the principles on which all are constructed are the same, and they do not differ much from one another. The objects to be attained are, to unite grinding and rubbing with mixing ; to ensure such a circulation of the pulp that the mercury shall be uniformly distributed without flouring ; and that the shoes and dies shall not be worn irregularly or unduly.

The so-called "combination" pan is an excellent amalgamator, and better than most, but the Wheeler pan is preferred as a grinder. The combination pan is usually 5 feet in diameter and about 3 feet 3 inches deep (Fig. 154). The bottom is of cast iron, and should have a flange cast on sufficiently high to reach above the level of the dies, to prevent leakage of mercury, and with a recess to take the bottom of the wooden staves which form the sides of the pan. The bottom of the pan is prolonged upwards in the form of a cone, through which the driving shaft (*g*) passes. The shaft carries a driver (*e*), to which the muller is fitted. The shoes (*d*), which correspond in number with the dies, are of hard iron, and are attached to the muller by dovetail projections and slots, in such a manner that they can be easily removed by reversing its motion. The muller can be raised or lowered by means of the hand wheel (*j*). The dies (*c*) are secured to the bottom of the pan by dovetail projections and sockets, and are so arranged that there are radial spaces between them and also a space between the sides of the pan and their outer edges. Their number varies from six to twelve.

On the sides of the pan are fixed several copper wings, which deflect the current, and prevent the pulp from rising too high at the sides, and also collect amalgam. The driving is by bevel gearing from below. The pan should have a steam jacket below for raising the temperature of the pulp to assist the amalgamation. In pans without steam jackets steam is introduced directly into the pulp, but this has the disadvantage of thinning it, and if exhaust steam is used, the oil which it contains causes the mercury to flour and hinders the amalgamation.

The Wheeler pan is also a 5-foot pan, but is much larger in W. Australia, where it is in extensive use for sliming gold ores. It differs chiefly from the combination pan in the shape of the shoes and dies, which have curved radial and bevelled sides instead of straight radial sides.

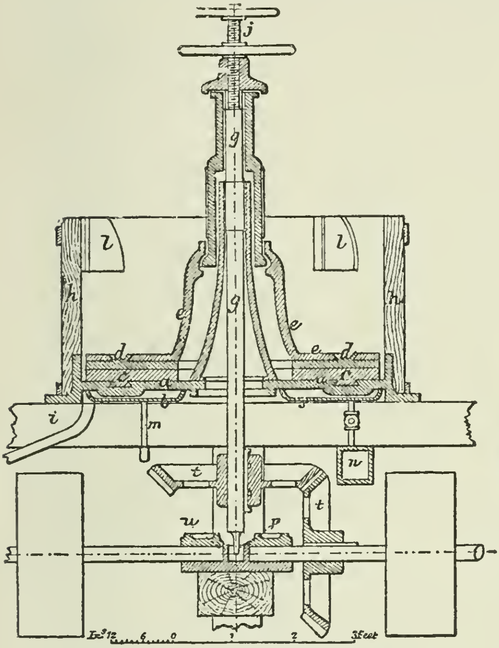

Fig. 154.—Amalgamation Pan.*

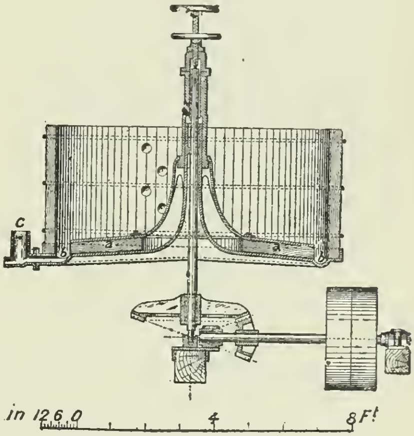

Fig. 155.—Settler.†

The Settler.—This is a large pan from 8 to 10 feet in diameter, with wooden sides and a cast-iron bottom (Fig. 155). The side is pierced with a line of holes, which can be closed with wooden plugs. The shoes are of wood, and in modern settlers are set in a ring. The bottom of the settler slopes towards a channel, which runs round the inside of the pan, to collect the mercury and amalgam. This channel connects with a cast-iron mercury well (c), fixed just outside the settler, having an outlet closed by a plug.

The object of the settler is to stir the pulp, which has been thinned with water, to bring about the coalescence of the globules of mercury and their subsidence. One settler should be provided for every two pans, as its work is performed in half the time required by a pan.

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* Rose, *Gold*, p. 225.

† Collins, *Silver*, p. 90.

The Clean-up Pan.—The Knox pan (Fig. 156) is a good form. This is a small cast-iron pan, 3 or 4 feet in diameter, with wooden shoes. It is used for cleaning the hard amalgam scraped from the shoes, dies, etc., of the amalgamating pans, and to separate iron and pyrites, etc., from dirty amalgam from the settler.

The Amalgam Safe.—As will be seen from Fig. 157, it consists of a sheet-iron vessel, in which is suspended a canvas bag for straining the amalgam, with a cast-iron well below to receive the mercury which drains from the bag.

It is kept locked to prevent theft.

In large mills the well is connected with an elevator, by which the mercury is raised and delivered into an iron tank, from which the pans are supplied.

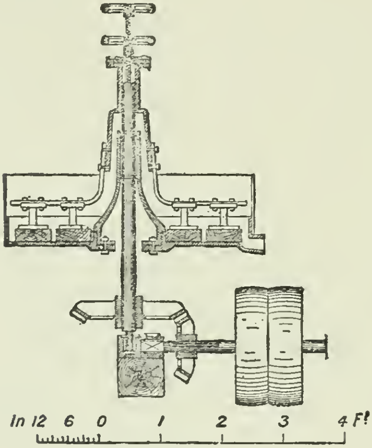

Fig. 156.—Clean-up Pan.[*]

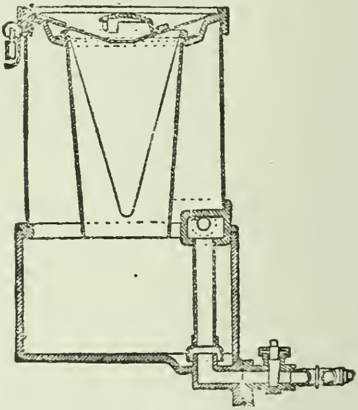

Fig. 157.—Amalgam Safe.[†]

Amalgam Retort.—A description of the retorts in use is given on p. 394.

The Process.—The charge for a 5-foot pan will be about 2,000 to 3,000 lbs. of ore.

Before charging, sufficient water to yield a pulp of the proper consistence is introduced. The ore is shovelled in, and during the charging the muller is revolved at from 60 to 90 revolutions per minute, to prevent "packing." It is then lowered, so that the shoes and dies almost touch. Steam is then introduced into the jacket to raise the temperature of the pulp and maintain it at about 160° to 200° F. (71° to 93° C.). The ore is ground, for about an hour or more, until it is reduced to a very fine pulp; then the mercury is added by squeezing through a canvas bag, the shoes having first been raised about ½ inch above the dies. The quantity of mercury charged varies at different mills, and not always in proportion to the richness of the ore. No regular rule appears to be followed. The amount ranges from 150 to 300 lbs. per charge.

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[*] Collins, *op. cit.*, p. 93.

[†] Collins, *op. cit.*, p. 94.

The revolution of the shoes is kept up for five or six hours, unless chloride ores are being treated, when a charge may be worked off in four hours. A large number of chemicals are employed, in many cases irrationally. Common salt and copper sulphate are, however, the most effective, and in some mills are the only chemicals used. These, too, must be used judiciously, and not in excess; if the last is in excess the bullion will be base, containing much copper. When the amalgamation is complete the pan is filled up with water to thin the pulp, the revolutions of the muller being decreased, and after five or ten minutes, as much as possible of the mercury and amalgam is drawn off into an iron pan. The pulp is then discharged into the settler, clean water being run into the pan during the discharge. At some mills the contents of two pans are discharged into the settler, and are worked for six or seven hours, but generally only the contents of a single pan are charged in, the time of working being then reduced to half the time required in the pan.

A clean-up of the pan takes place once or twice a month, when the shoes and dies are taken out and scraped, and the whole surface of the pan cleaned, to remove adherent hard amalgam, and also any graphite which may have been set free.

When the pulp is being discharged into the settler the shoes of the settlers are revolved, and special care must be taken to regulate their height, the number of revolutions, and particularly the thickness of the pulp, so that the mercury and amalgam will separate and settle. The revolutions will range from ten to twenty per minute, and the height of the shoes at first will be 6 or 8 inches, and at the last nearly touching the bottom.

When the amalgam and mercury have settled, the top discharge hole is opened, and the lighter part of the pulp allowed to flow off; the other holes are then opened in succession, and all the material except mercury and amalgam run off. The pulp should be discharged over a riffle, or blanket sluice, or sent to tables, to separate pyritic concentrate which sometimes carries payable gold.

The mercury and amalgam are dipped out from the mercury well, and finally tapped out by removing the plug from the outlet pipe. In some large mills the mercury and amalgam were led directly to the amalgam safe by means of a pipe attached to the outlet of the mercury well. A considerable amount of impure amalgam, mixed often with heavy sulphides, remains behind in the settlers until the clean-up, which takes place once a week. The mercury and amalgam are first carefully washed from sand and pyrites, and then taken to the amalgam safe, where it is strained through a canvas bag. The bag is afterwards squeezed and solid amalgam obtained.

The amalgam is retorted, and the silver obtained as bullion, as described on pp. 394-396.

Clean-up.—The hard amalgam, obtained by scraping the shoes, dies, and iron work of the pans, and the dirty amalgam mixed with pyrites and iron from the clean-up of the settler, are charged into the clean-up pan and well stirred with hot water, some fresh mercury being added. The sulphides and iron rise to the surface of the amalgam, and are skimmed off. The iron is sometimes removed with a magnet. The cleaned amalgam is sent to the amalgam safe, and charged into the filter bag.

The percentage of extraction varies with the percentage of silver chloride present in the ore, and the amount and nature of the impurities. With much silver chloride 85 to 90 per cent. of the silver may be extracted, but otherwise not more than 60 to 70 per cent., or even less.

The loss of mercury varies from ½ lb. to 3 lbs. per ton of ore.

This loss is chiefly due to handling, "sickening," and "flouring." The loss from handling may be minimized by connecting the settlers with the amalgam safe by pipes, raising the mercury from the receiver of the safe by the elevator to a mercury storage tank, and distributing it from this to the pans also by pipes.

Mercury is said to be "sickened" when it will not amalgamate and its globules will not unite. This may be brought about by the presence of talcose or clayey matter, lead, arsenical and antimonial ores in the charge, by graphite from the pan, and by grease, all of which by coating the globules prevent their coalescence.

Mercury is said to be "floured" when it is in such a fine state of division that it resembles flour, and the minute particles will not coalesce. In this condition it passes away in the tailings. Flouring is caused by over grinding in the pans, by the presence of the substances that cause sickening, which is often the preliminary stage of flouring.

The remedies for both sickening and flouring are :—

(*a*) Keep all oil and grease out of the charge.

(*b*) The mercury to be kept in active condition with KCy and sodium amalgam.

(*c*) Clean the mercury from time to time by covering it with dilute nitric acid, 1 part of acid to 3 parts of water.

(*d*) Distil the mercury with iron filings and lime, or with alkaline nitrates, or sodium peroxide.

Lead ores, in addition to producing sickening of the mercury, form a pasty amalgam, which is readily washed away, and causes a loss of silver.

Copper ores make the bullion low in fineness. Manganese oxides greatly increase the loss of mercury.

The reactions which occur in the Washoe process for the silver chloride in the ore, when no chemicals are used, are :—

$$2AgCl + Fe = 2Ag + FeCl_2.$$
$$2AgCl + 2Hg = 2Ag + Hg_2Cl_2.$$

The latter, however, can only take place to a limited extent, or the loss of mercury as Hg_2Cl_2 (calomel) would be very much greater than it is. The real reaction being—

$$2AgCl + Fe + xHg = Ag_2xHg + FeCl_2.$$

The iron is derived from the finely divided iron from the wear of the shoes, dies, and stamps; the iron of the pan itself also takes part in the reaction.

When copper sulphate and common salt are used, the yield of silver is increased, and the amalgamation is more rapid. In these cases the common salt acts as a solvent of the AgCl, and thus facilitates the reduction of the silver by iron and copper. Copper, precipitated from the sulphate by iron, and iron are thus the chief reducing agents in the process, the reactions being—

$$\begin{aligned} CuSO_4 + 2NaCl &= CuCl_2 + Na_2SO_4. \\ CuCl_2 + Fe &= Cu + FeCl_2. \\ 2AgCl + Cu + xHg &= Ag_2xHg + CuCl_2. \\ CuCl_2 + Cu &= Cu_2Cl_2. \end{aligned}$$

When argentite is present also, it has been supposed that it is reduced by mercury, the mercury sulphide being lost—

$$Ag_2S + Hg = 2Ag + HgS.$$

But it is more probable that it is reduced by the copper precipitated by iron from the sulphate or chloride, as follows :—

$$Ag_2S + Cu = 2Ag + CuS.$$

The CuS is rapidly oxidized to sulphate, and again takes part in the reactions.

Other reactions are—

$$\begin{aligned} Ag_2S + Cu_2Cl_2 &= 2Ag + CuCl_2 + CuS. \\ Hg_2Cl_2 + Cu &= 2Hg + CuCl_2. \end{aligned}$$

The precipitated copper remaining after the reduction of the AgCl and Ag_2S amalgamates with the mercury, and lowers the fineness of the bullion.

In Fig. 158 is shown the arrangement of a silver mill in which the Washoe process was carried on. The chief parts of the plant are :—

Grizzly.
Rock breaker and bin.
Stamps.
Collecting and settling boxes.
Pans.
Settlers.
Amalgam safe.
Mercury elevator.
Mercury tank.
Retorting furnace.
Melting furnace.

(*c*) **The Boss Continuous Process.**—The ordinary pan amalgamation process is intermittent, as the ore from the stamps has to be collected and charged into the pans at intervals. In the Boss process the material from the stamps flows continuously through the amalgamating pans and settlers.

A peculiar feature of the Boss process is the provision of a series of small 4-foot flat-bottomed pans, for further grinding the pulp before it passes from the stamps to the amalgamating pans.

In some new plants the pulp from the grinding pans first goes into a mixer, resembling a settler, in which it is mixed with chemicals, as salt and blue stone ; in others, the chemicals are charged into the first two amalgamating pans. Fig. 159 represents the arrangement of a mill for carrying on the process.

The pulp from each of the ten stamps A is passed into one of a pair of grinding pans B, from which it passes to the other, and thence into the common launder leading to the mixer, where there is one, otherwise, to the first of the amalgamating pans C, and then flows successively from pan to pan, and settler to settler, through the whole series of nine or ten amalgamating pans and four settlers D, D, D, D. The tailings are led from the last settlers to settling cones, and then to vanners or tables E to collect pyritic concentrate.

The mercury is charged into the pans by pipes leading from the mercury cistern. The amalgam accumulates in bowls attached to the front of each

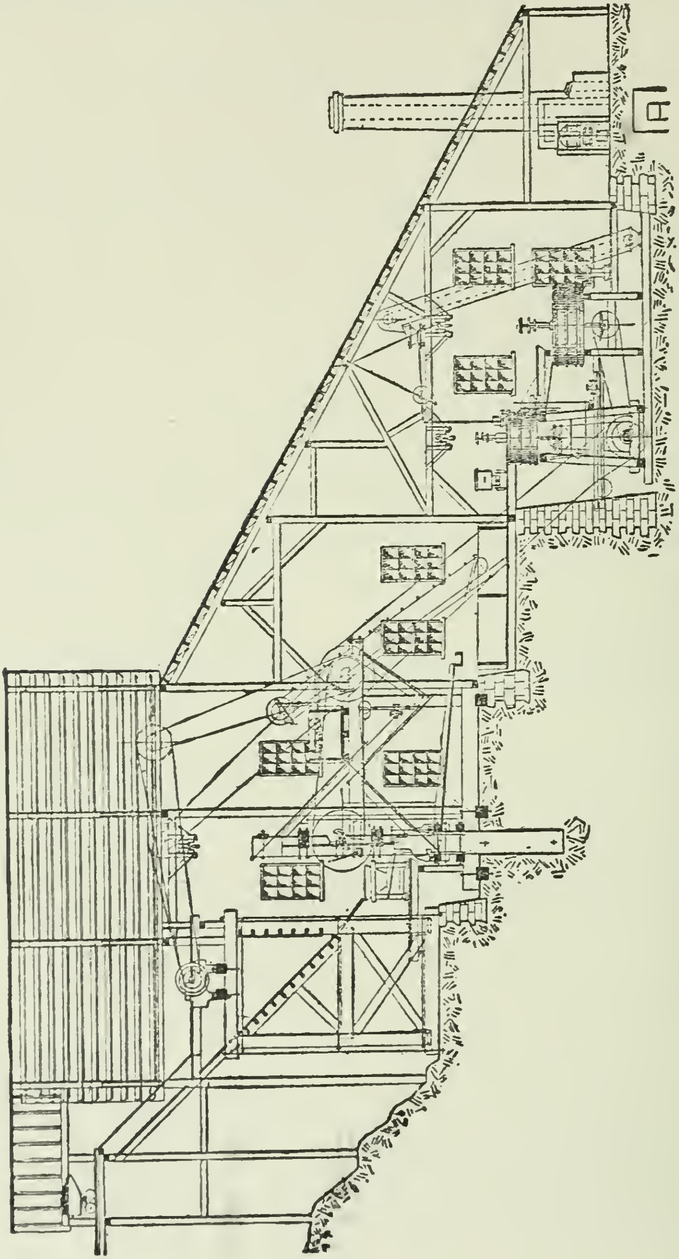

Fig. 158.—Old Washoe Mill. General Arrangement. (Collins, *op. cit.*, p. 103.)

pan and settler, and is drawn off from time to time into an iron pipe, by which it is led to the strainer in the amalgam safe.

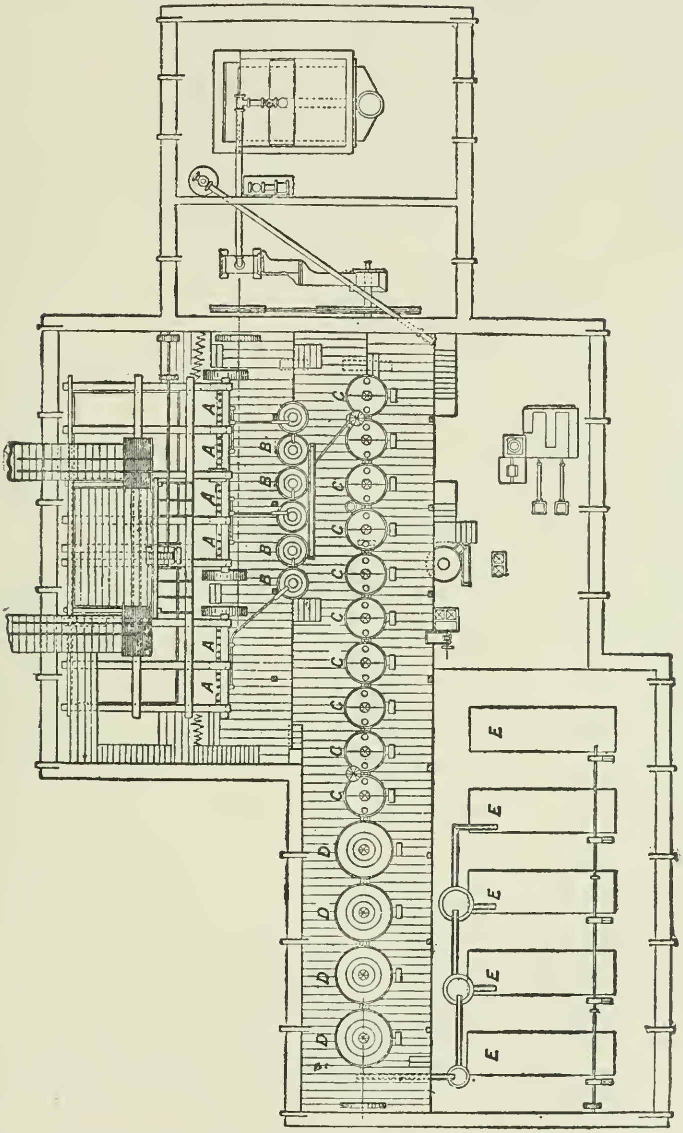

Fig. 159.— Plant of Boss Process. (Collins, *op. cit.*, p 109.)

Any pan or settler can be shut off from the series when necessary, the flow of the pulp being diverted to the next one by a siphon. The following advantages are claimed for the process :—

1. The slime as well as the sand is treated, as all the pulp goes to the pans.
2. Saving in labour, in charging, in feeding in mercury, and in collecting amalgam.
3. By using grinding pans, the ore can be put through coarser screens at the battery.
4. Less loss of mercury than in the ordinary process, as the pulp is thinner, and hence there is better separation.

It is claimed that any ore adapted for pan amalgamation can be worked more successfully by this continuous process than by any other.

Substances which interfere with the Pan Process—*Grease, Talc, and Kaolin* —Coat the globules of mercury, and prevent amalgamation.

Copper Ores.—Do not interfere, except by making the bullion low in fineness.

Lead Ores.—Do not resist amalgamation, but cause a loss of silver by forming a pasty amalgam which is readily washed away, and a loss of mercury by causing it to " sicken."

Zinc Blende.—Effect doubtful. Said to cause the mercury to sicken.

Ores containing Arsenic and Antimony.—These ores are unsuitable for the Washoe process, as they cause great losses from both " sickening " and " flouring " of the mercury, and imperfect extraction of the silver. They must hence be subjected to chloridizing roasting before amalgamation.

Manganese Oxides.—Cause great loss of mercury and low extraction of silver. Oxygen is supposed to be given off and the mercury oxidized.

Chloridizing-Roasting of Silver Ores.—When the silver occurs in ores as sulphide, sulph-arsenides, sulph-antimonides, and in fahlerz—the so-called rebellious ores—and when the silver mineral is in isomorphous association with other sulphides, as blende, pyrites, galena, and the like, chloridizing-roasting is necessary for the preliminary preparation of the ores for amalgamation.

Simple roasting may sometimes be sufficient, but a more perfect amalgamation is obtained after roasting with salt, and the latter is commonly practised, notwithstanding the losses of silver by volatilization.

Chloridizing-roasting is also necessary in certain lixiviation processes, such as the Augustin, von Patera, etc.

Chloridizing-roasting consists in roasting the ores with common salt, the object of the process being to convert the whole of the silver into chloride, and as little as possible of the other metals, with the exception of copper. This is effected by the decomposition of the salt ($NaCl$) at the temperature and in the atmosphere of the furnace by sulphates and by silica, yielding chlorine and hydrochloric acid, which by their action on native silver, silver sulphide, sulph-arsenides, and sulph-antimonides form silver chloride. The ore is first crushed dry to pass through a mesh of about 20 to 40 holes to the linear inch. If much argentiferous blende or galena is present, it must be crushed finer than when it contains only pyrites. If the ore is crushed wet it must be dried, and this is best done in a revolving cylindrical furnace with continuous discharge.

Stamps, rolls, or Chilian mills are all in use for crushing, stamps being preferred for crushing through 30 to 40 mesh, and rolls, or sometimes Chilian mills for coarser sizes, also when the ore has to be leached, as they produce less slime and give a more granular product.

The best results in chloridizing-roasting are obtained when the ores contain from 3 to 8 per cent. of sulphur as pyrites. When much zinc blende or galena is present the operation is prolonged and the loss of silver is greatly increased. If an ore contains less than 3 per cent. of sulphur, sufficient pyrites must be obtained to bring up the sulphur content to 3 or 4 per cent., and if much calcspar is present more will be required.

When the ore contains more than 8 per cent. of sulphur, it should be first partly roasted before the addition of the salt, otherwise a considerable quantity of chlorides of the base metals present will be formed. The most suitable furnaces for chloridizing-roasting are reverberatory furnaces, either hand-worked (p. 23), or with mechanical rabbles (pp. 25 to 37) for large plants. Of the latter, the Brown furnace (p. 25) and its modifications, also the Wethey (p. 27), Pearce turret (p. 33), and the Ropp (p. 29), are all effective, and especially so as the addition of salt may be made in them at any time after the excess of sulphur has been roasted off.

The Stetefeldt furnace and the Brückner cylinder have also been in use to a considerable extent in America, but the former furnace is not satisfactory when the ores contain over 15 per cent. of sulphur, and the latter has a tendency to ball the ore.

Revolving cylindrical furnaces with continuous discharge, as the White and White-Howell types, are also employed, but they have one great disadvantage—*i.e.*, that the salt has to be mixed with the ore before charging.

The Process as conducted in Reverberatory Furnaces.—The ore is charged into the furnace at the end furthest from the fire-place, where the temperature is low, and is gradually moved with frequent stirring with rabbles towards the hotter parts of the furnace bed. The pyrites are oxidized, SO_2 being given off, and sulphates of iron and copper are formed. At this stage, and before the decomposition of these sulphates, the salt is added, and the charge gradually moved nearer the fire-bridge; chlorine and some hydrochloric acid are given off, and the silver is converted into chloride.

The chloridized ore is now raked out of the furnace. Perfect chloridization is not usually attained, and a greater or less amount of the silver may not have been chloridized; the roasted ore is, therefore, allowed to cool gradually in heaps for a day or more, when further chloridizing goes on, and may increase the amount of silver chloride by 10 to 25, or sometimes to even 40 per cent.

Wetting or damping the heap of roasted ore will increase the chlorination when the ore is cupriferous, the copper chlorides reacting with the undecomposed silver sulphide, but it should not be done until the ore has somewhat cooled.

The loss of silver in chloridizing-roasting, taking a general average of all the various plants and localities, is little under 5 per cent. (*Collins*). The effects of As, Sb, Bi, and other volatile elements are to increase this loss, but they have not been systematically investigated.

The chief conditions for successful chloridizing-roasting may be summarized as follows:—

1. The ore should contain from 3 to 8 per cent. sulphur in the form of pyrites.

2. If the ore contains less, pyrites should be added to bring up the sulphur contents to 3 or 4 per cent.

3. If it contains more than 8 per cent. sulphur, some must be burned off before adding salt.

4. If much calcspar (calcium carbonate) is present, and the ore is intended for leaching, a considerable quantity of pyrites must be added to convert most of the lime into sulphate, as the effect of lime on the cooling floor is to reduce AgCl to Ag, and this is not dissolved in the leaching processes.

5. The ore must be so roasted that the iron and copper of the pyrites be, as far as possible, converted into sulphates before the addition of the salt.

6. A large excess of salt should not be used. The quantity required must be determined by experiment; it varies from 3 to 15 per cent. of the weight of the ore, 5 to 6 or 8 per cent. being common.

7. Finally, the iron should be in the form of ferric oxide, the zinc as oxide and basic sulphate, the lead as oxide and sulphate, and the copper as oxide and chloride.

8. Slow roasting, at as low a temperature as possible, is a golden rule in chloridizing-roasting. The roasted ore should be allowed to cool in heaps for one or two days, when the silver is further chloridized.

The reactions which take place in chloridizing-roasting are complicated, but the following are the most important. Before the salt is added the roasting is oxidizing, thus—

$$\begin{aligned} 3FeS + 11O &= Fe_2O_3 + FeSO_4 + 2SO_2. \\ 2CuS + 7O &= CuO + CuSO_4 + SO_2. \end{aligned}$$

If sulph-arsenides or sulph-antimonides are present they are oxidized, and part of the As and Sb is volatilized. On the addition of the salt the sulphates react with it, chlorine being set free.

$$2NaCl + 2FeSO_4 + O = 2Cl + SO_2 + Na_2SO_4 + Fe_2O_3.$$

Further—

$$\begin{aligned} 2FeSO_4 + O &= 2SO_3 + Fe_2O_3. \\ CuSO_4 &= SO_3 + CuO. \end{aligned}$$

The SO_3 set free by this decomposition of these sulphates by heat acts on the salt thus—

$$2NaCl + 2SO_3 = 2Cl + SO_2 + Na_2SO_4.$$

Copper sulphate is decomposed by NaCl—

$$CuSO_4 + 2NaCl = Na_2SO_4 + CuCl_2.$$

Some hydrochloric acid is also formed in the presence of steam.

$$2NaCl + SO_3 + H_2O = 2HCl + Na_2SO_4;$$

and by the action of SiO_2, thus—

$$2NaCl + SiO_2 + H_2O = 2HCl + Na_2SiO_3.$$

The chief reagent in the process is, however, chlorine, and by its action on silver sulphide, sulph-arsenide, and sulph-antimonide, they are converted into silver chloride.

Any hydrochloric acid which may be formed will convert oxides, sulphates, arsenates, and antimonates into chlorides.

The silver sulphide is acted on as follows:—

$$\begin{aligned} Ag_2S + 4SO_3 &= Ag_2SO_4 + 4SO_2. \\ Ag_2SO_4 + 2NaCl &= 2AgCl + Na_2SO_4. \\ Ag_2SO_4 + CuCl_2 &= 2AgCl + CuSO_4. \end{aligned}$$

(*d*) **Amalgamation in Pans with Previous Roasting**—*The Reese River Process.*—The process is so-called as it was first introduced in that district. It is now obsolete. The ores contain sulph-arsenides, sulph-antimonides, tetrahedrite, and base metal sulphides, and hence cannot be treated direct by pan amalgamation, as in the Washoe process, but must first be roasted with salt, as previously stated. If the above interfering substances are only present in small amounts simple roasting without salt may, however, suffice.

The ores are dry-ground and chloridized, as described under "Chloridizing Roasting" (p. 390). They are then treated in amalgamating pans in exactly the same way as in the Washoe process, but the pans have wooden sides, as iron is so readily acted on by chlorine.

Copper sulphate is added, during the working of the charge in the pans, to reduce any Ag_2S which may not have been decomposed in the roasting, and generally a little salt in addition to that already in the chloridized ore. The time of working a charge is about six hours, as in the Washoe process.

The percentage of silver recovered is very variable; it depends on the character of the ore, but is greater than in raw ore amalgamation, and often reaches 85 or 90 per cent. The chief loss is in the chloridizing-roasting, and on this account, and the cost of the roasting, the process has been given up.

The ore is prepared for amalgamation as follows:—It is passed over a grizzly, the coarse going to the rock breakers, and thence to a revolving cylindrical drier, the fines going direct to the drier. From the drier the ore passes to the dry stamps. The crushed material is taken by conveyors to a White-Howell furnace, in which it is roasted with salt and then delivered to the cooling floor, whence it is fed into the amalgamating pans.

The chief reactions which occur in the process of amalgamating the chloridized ore in pans are as follows:—

$$\begin{aligned} 2AgCl + Fe + xHg &= Ag_2Hg_x + FeCl_2. \\ 2AgCl + Cu + xHg &= Ag_2Hg_x + CuCl_2. \\ CuSO_4 + 2NaCl &= CuCl_2 + Na_2SO_4. \\ CuCl_2 + Fe &= Cu + FeCl_2. \end{aligned}$$

Metallic iron from the interior of the pan, and the fine particles of iron from the wear of the shoes and dies, are important agents in reducing the AgCl. This iron also reduces Cu from the $CuCl_2$ and any $CuSO_4$, the Cu thus reduced becomes diffused through the pulp, and acts as a reducing agent on the AgCl, setting free metallic Ag. The Ag thus set free in these reactions combines with the Hg, forming an amalgam, and this amalgam is held in suspension by the excess of Hg.

If any Ag_2S is present it is decomposed by mercury in the presence of $CuSO_4$. Too much $CuSO_4$, however, should not be used, as after all the AgCl is decomposed the excess of Cu amalgamates with the Hg, and thus may form a low-grade bullion, as stated on p. 387.

The Combination Process.—When a silver ore contains a fair proportion of silver chloride and sulphide, which are amalgamable, together with argentiferous and auriferous sulphides, such as galena, copper pyrites, blende, and arsenical and antimonial or manganese minerals which are non-amalgamable, the so-called "combination" process is suitable for their treatment.

The process consists of the following operations :—

1. The ore is wet-crushed in stamps with 30-mesh screens, in the usual way, the pulp being passed over amalgamated apron plates, to catch any free gold which may be present.

2. The pulp from the stamps is distributed to Frue vanners or concentrating tables, where the sulphides and heavy minerals are separated and collected. As these minerals are not only non-amalgamable, but interfere seriously with pan amalgamation by causing loss of mercury and the production of a low-grade amalgam, their separation at this stage is of the utmost advantage.

The concentrates obtained which still contain gold are almost always sold to smelters. They may, however, be roasted with salt and then amalgamated.

3. The tailing from the vanners or tables now goes to the collecting tanks and amalgamating pans of a Washoe plant, where they are treated exactly as described under the "Washoe Process" (p. 382).

The applicability and advantages of the combination process are summarized by Collins,* as follows :—

(1) Easier and more perfect saving of sulphides.
(2) Lower final tailings.
(3) Cleaner bullion from pans.
(4) Less loss of quicksilver.

The process is applicable to all ores carrying argentiferous or auriferous sulphides, but more particularly to the following :—

(1) Those in which the sulphides, though comparatively small in amount, are rich, say 50 ozs. to the ton, or upwards.

(2) Those in which the sulphides, though poor, are yet worth treating, and where they constitute more than 5 per cent. of the weight of the ore.

Retorting and Melting Silver Amalgam—*Retorting Amalgam.*—The amalgam from the various amalgamation processes will generally contain about 20 per cent. of silver, unless copper or lead have been present in the ores, or an excess of copper sulphate has been used in the amalgamation. The amalgam, after it has been strained through canvas and been well squeezed, is made into small balls or flat cakes.

In Mexico at a few small works a very simple arrangement of old quicksilver flasks is employed for retorting. From 16 to 20 flasks are taken, and the bottoms cut off from half the number, and the necks from the remainder. The latter are fitted into holes in an iron plate set over a tank of water, into which they dip and serve as receivers for the condensed mercury. The former act as retorts, being set and luted over the receivers. They are contained within a brick chamber closed at the top by an iron plate, and having an external fire-place. After they have been filled with small balls of amalgam and luted to the receivers, a fire is made in the fire-place. The mercury is volatilized and condenses in the flask receivers, which are kept cool by water circulating in the tank. This method is extremely simple, and only mercury flasks are required both for distillation and condensation.

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* Collins, *The Metallurgy of Silver*, p. 133.

At all the silver mills in the United States, and at most mills elsewhere, the retorting is effected in horizontal retorts. A typical retort and condenser is shown in Fig. 160.

The retorts are of cast iron, and range in size from 2 feet 6 inches in length and 10 inches in diameter to 4 or 5 feet in length by 10 to 14 inches in diameter. They are set in brickwork, and are supported at several points in their length by fire-clay curved supports, to prevent sagging when hot. At one end they are closed by a removable door, and at the other is an opening, to which the condenser is attached by a wrought-iron tube. The condenser is of the Liebig type, consisting of a wrought-iron tube enclosed in an outer tube, the water for cooling circulating through the intervening space. The lower end of the inner tube fits into a sheet-iron cylinder, which just dips into the water in the vessel for receiving the condensed mercury. This is necessary to prevent water being sucked back into the retort and causing an explosion. The top of the inner tube should be fitted with a four-way connection for the purpose of clearing out any obstruction which may be caused by amalgam accidentally carried over. A hood is fitted over the front of the retort to carry off the mercury fumes. The charge for a retort varies from 200 to 2,000 lbs. of amalgam.

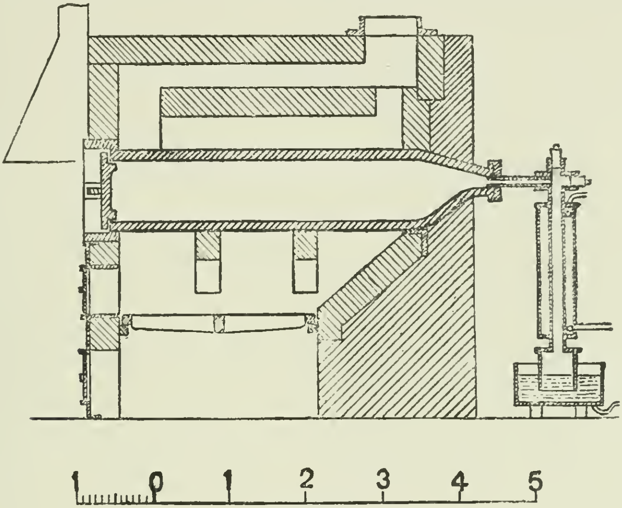

Fig. 160.—Amalgam Retort.

The balls or cakes of amalgam are best charged into the retort on sheet-iron trays which have been previously dipped in lime wash or thin clay luting to prevent adhesion of the silver.

When the trays carrying the charge have been introduced, the door at the mouth of the retort is clamped and luted. The fire is lighted, a gentle heat is kept up for some time, but towards the end is gradually increased to redness. The mercury distils over and is condensed in the condenser. The retort is then allowed to cool, and the spongy silver removed.

The operation generally requires about eight to twelve hours. The spongy silver is melted, usually in plumbago crucibles, with a little borax, sometimes together with nitre, and cast into ingots of about 1,000 ozs. in iron moulds. The crucible on removal from the furnace must be allowed to stand for some time, the metal being gently stirred, to allow oxygen to escape, and the pouring must be done at the lowest possible temperature, otherwise " sprouting " will take place.

(2) **The Cyanide Process as applied to Silver Ores.**—The cyaniding of silver ores was formerly considered to be attended with too many difficulties to be carried out economically on a large scale. The success of pan amalgamation also prevented its introduction in the silver districts of the United States. But in Mexico, where that process could not always be conducted with profit on the low-grade silver and gold ores, which are so abundant, and the *patio* process was being abandoned on account of its cost, there was a promising field for the adoption of cyaniding in several districts. It was hence in Mexico, at El Oro, that the real pioneer work in the adoption of the process was carried out, and it now is in successful operation at all the important mines in the country.

The old time-honoured *patio* process has been abandoned, and at the present time Mexico occupies a prominent position in the development of the cyanide process. The low-grade ores, which formerly could not be worked economically, and the tailings left by the old crude methods of treatment, are now being worked with great profit. The process is, in fact, the most economical and satisfactory for the treatment of the low-grade silver and gold ores as they occur in Mexico. It has displaced the *patio*, pan amalgamation, and other processes, as previously stated, at all the important mills, and is destined to play a very important part in the metallurgy of silver. It is especially suitable for ores containing silver chloride, bromide, iodide, and sulphide, all of which are soluble in solutions of potassium cyanide. Native silver is also soluble, but, unless in very small particles, requires too long a time for solution. The sulph-arsenides and sulph-antimonides are also soluble, but much less so than the compounds of silver just mentioned.

Oxygenation of the charges is absolutely necessary to ensure the solution of the silver mineral, and is more important in the treatment of silver ores than in that of gold ores. Silver ores also require stronger solutions, and a longer treatment than gold ores, and the consumption of cyanide is greater.

As regards crushing and grinding, stamps and tube mills form the standard equipment for cyanide plants, but metallurgists are not altogether unanimous as to the degree of fineness to which the ore should be reduced by these machines respectively. The best extraction is obtained when the whole of the ore is slimed, and that method is in use in the newest mills. Payable amounts of silver can, however, be extracted from some ores, without incurring the expense of fine grinding in tube mills, the sand and slime from the stamps being treated separately, the former by leaching and the latter by agitation, as in cyaniding gold ores. The leaching of the sands, however, occupies a very long time, and the extraction is lower than when the ore is slimed. For classification, the spitzkasten and spitzlutte are gradually giving way to the conical and mechanical classifiers.

Continuous treatment by cyanide solutions is now being aimed at, and is in practice at many works, the agitation being performed in Brown, Dorr, Trent, or other agitators. The best system of filtration is by no means definitely settled, hence in some mills we find vacuum filters, in others filter presses, both of the intermittent types; whilst in some of the latest mills Merrill's presses have been erected. In one or two of the newest mills continuous counter-current decantation has been adopted, filtration being dispensed with, see p. 398. Deficiency of oxygen is one of the chief leaching troubles, the remedies being, in the case of sand, either transference from one vat to another, or the introduction of the cyanide solution alternately on the top and at the bottom of the charge.

Lead acetate is generally used in silver cyanide plants for precipitating soluble sulphides, as silver will not remain in solution in their presence. An excess must be avoided as it consumes cyanide, and lead will be precipitated on the zinc, giving rise to base bullion.

The formation of white precipitate, which may cover the zinc and hinder precipitation, is usually the result of too little or too much lime in the solution. In silver treatment plants, where lead acetate is used, there is rarely any difficulty from white precipitate.

Among the chief causes which impede the extraction of silver by the cyanide process is the occurrence of the metal as native silver and silver sulphide, and as sulph-arsenides and sulph-antimonides, such as pyrargyrite, proustite, etc. None of these minerals are readily soluble in cyanide solutions; further, they resist the action of oxidizing agents, and give rise to the formation of soluble sulphides.

The operations at many plants are, in outline, as follows:—

1. The ore, after being broken in rock breakers, is crushed in a stamp battery, with or without cyanide solution, to pass screens varying generally from 4 to 16 mesh.

2. When the ores contain argentiferous and auriferous pyrites, the pulp is usually sent to concentrating tables for their separation and collection. The concentrate at the majority of the mills is still sold to smelters, but its treatment by cyaniding is receiving attention, and as soon as an efficient and profitable method has been worked out it will be dealt with at all the mills themselves.

3. The pulp is then classified in classifying cones, or in special classifiers, and sent to tube mills.

4. In the tube mills it is slimed, and then passed through cones or other classifiers, and the coarse returned to the tube mills.

5. The slime from the tube-mill classifiers is thickened in Dorr thickeners.

6. The thickened slime is then agitated in Brown (Pachuca), Dorr, Trent, Hendryx, or other vats, generally with 0·3 KCy solution. Heated solutions are usually employed in Nevada and Mexico.

In Mexico, as at other mining centres, there is quite a difference of opinion regarding the efficiency of agitators, the Trent being used at the MacNamara, Montana, and West End; the Hendryx at the Montana; Brown vats at the new Belmont Mill; Dorr vats at the new Nevada Packard Mill; and ordinary mechanical agitators and air lifts at the Belmont and Tonopah and at Millers (Tonopah, Nevada).

7. The slime then passes to vacuum filters, or filter presses, the resulting cakes going to the dump.

8. The solutions from the presses, or filters, are passed through zinc boxes, or are treated with zinc dust.

9. The silver and gold precipitate is converted into bullion, as described, p. 334.

The percentage of silver and gold extracted varies considerably. At Pachuca it reaches 91·4 per cent. of the silver and 97·0 per cent. of the gold, including the bullion obtained from the concentrate. At the Esperanza Mining Company, El Oro, Mexico, the extraction is, silver 60 per cent., gold 90 per cent. At other mills the extraction generally ranges between these percentages.

In the installation of the newest silver mills and the re-equipment of others, the following is an outline of the practice which has been adopted:—

1. The ore after being broken in rock-breakers is further reduced to $\frac{3}{8}$ inch.

2. It is then finely ground in tube mills.

3. The product from the tube mills flows to a Dorr classifier, the coarser being returned to the tube mill, on the closed-circuit system, until the whole is ground to 200 mesh.

4. The overflow from the classifier is led to a Dorr thickener (No. 1), the solution from which after being clarified is pumped through a Merrill precipitation press, where the Ag and any Au present is precipitated by zinc dust.

5. The thickened pulp from the thickener is then treated by continuous agitation with cyanide in Brown, Dorr, or other agitators, set in series.

6. From the agitators the pulp flows to a series of Dorr thickeners for treatment by the continuous counter-current decantation method (see pp. 409, 410), the solution and its diluents travelling through successive thickeners to the first thickener (No. 1), or to a sump tank, and the pulp in the opposite direction.

7. The pulp from the final thickener is discharged to waste, or may be treated in vacuum filters, but these are being discarded.

At a few of the older mills in Mexico the ore is crushed by stamps with 20 to 30 mesh screens, and the pulp treated on tables for the separation of pyritic concentrate.

The tailing from the tables is separated into sand and slime, partly by cone classifiers, and finally by ordinary overflow collecting vats.

At these mills the overflow collecting vats, with filter bottoms, are charged by Butters and Mein distributors in the usual way. When full, the sand is allowed to drain, and is then discharged through the bottom opening by shovelling, or by a Blaisdell excavator, upon a travelling belt, by which it is conveyed to the leaching vats. Aeration of the charge is thus effected. Lime is generally fed to the sand, on the belt, to the amount of about 6 lbs. per ton. As soon as the leaching vat has received its charge, 100 to 300 tons.

and the sand has been levelled, the treatment begins. This varies more or less at different mills, chiefly in the mode of adding the KCy solutions.

The time of leaching the sand ranges from twelve to seventeen days, and the strength of the strong solutions from 0·4 to 0·55 per cent. KCy, the weak solutions usually being of 0·1 per cent. At the Guanajuato Reduction Company's Mill, the strong solution is run on every twelve hours, until it stands 4 inches above the level of the sand, the outlet being closed for two hours, then opened, and the vats allowed to drain. This gives fairly good aeration between the additions of solution. This is continued for seventeen days, and is followed by two days' continual washing and one day of draining.

At other mills the strong solution is applied more frequently for only twelve or fourteen days, and a wash of weak cyanide, 0·19, is given before the water wash.

The method of leaching the sand and slime separately is unsuitable for ores in which the silver sulphide is finely disseminated through the gangue, and sliming of the whole of the ore is necessary to obtain a satisfactory extraction.

Reactions.—The reactions involved in the cyaniding of silver ores are still only imperfectly understood, but the following account represents the conclusions which thus far have been more or less accepted. The solution of silver and silver sulphide in potassium cyanide solution takes place respectively in accordance with the following equations :—

$$(1)\ 2Ag + 4KCy + H_2O + O = 2KAgCy_2 + 2KHO.$$
$$(2)\ Ag_2S + 4KCy = 2KAgCy_2 + K_2S.$$

When a certain amount of silver has been dissolved in equation (2) equilibrium is established, and no more passes into solution. The amount of silver which can be dissolved, and remain in solution without being precipitated as sulphide, depends on the amount of free KCy present.

In practice, however, according to Caldecott, many ounces of silver existing as sulphide in the ore can be dissolved, as the potassium sulphide is converted, according to the following equations, into other compounds, which do not preclude the further solution of silver :—

$$(3)\ 2K_2S + 4O = K_2S_2O_3 + K_2O.$$
$$K_2S_2O_3 + K_2O + 4O = 2K_2SO_4.$$
$$(4)\ K_2S + KCy + O = KCyS + K_2O.$$

These reactions all involve absorption of oxygen, and indicate the utility of aeration.

Further, the formation of large amounts of alkaline sulphide may be prevented by the addition of lead acetate, or soluble salts of lead, or litharge (according to Eye), thus—

$$(5)\ PbAc_2 + 4KHO = K_2PbO_2 + 2KAc + 2H_2O.$$
$$K_2S + K_2PbO_2 + 2H_2O = PbS + 4KHO.$$

$$(6)\ K_2S + PbO = PbS + K_2O.$$
$$PbS + KCy + O = KCyS + PbO.$$

From reactions (5) and (6) with lead present as plumbite (K_2PbO_2), or as oxide, it will be seen that a limited quantity of lead salt serves to remove an indefinite quantity of soluble sulphide, but only at the expense of free cyanide, which is converted into useless sulpho-cyanide (*Caldecott*).

According to Clennell's experience, for a given ore, a maximum increase in the extraction of silver was obtained in the presence of a certain proportion of lead acetate or litharge ; as this proportion was exceeded, the amount of silver dissolved diminished progressively, and was ultimately lower than when cyanide alone was used.* The addition of salts of mercury is sometimes made to decompose soluble sulphides, and it has been claimed that their presence facilitates the solution of minerals, such as proustite, pyrargyrite, and the like, but this has not been definitely established.

Precipitation of the Silver.—The silver is precipitated from the cyanide solutions in zinc boxes or by zinc dust as described, under " Gold," pp. 325 and 328, except that the precipitate is not subjected to treatment by sulphuric acid, and provision has to be made for its larger bulk. The precipitate is dried in shallow pans, heated in a muffle furnace, or by steam, or by electricity at the Tigre Mill (Mex.), and after drying is melted with fluxes in crucibles in oil-fired tilting furnaces. Aluminium and sodium sulphide are also used as precipitants.

An interesting example of the treatment of the precipitate obtained by zinc-dust precipitation is the method practised at the Tigre Mill, Sonora, Mexico.†

The precipitate has the following composition :—Au 0·3 per cent., Ag 63·13 per cent., Cu 1·5 per cent., CuO 3·14 per cent., Zn 2·0 per cent., ZnO 3·23 per cent., SiO_2 11·6 per cent., Al_2O_3 5·7 per cent., Fe_2O_3 1·3 per cent. After removal from the presses it is dried by electrical heating in a series of superimposed shallow pans, under which the resistance coils are placed.

After drying it is melted in crucibles in oil-fired tilting furnaces, having been first mixed with fluxes in the following proportions :—Precipitate 100, borax 5, silica 5·7, sodium bicarbonate 9·1, fluorspar 0·6. This mixture is charged into the crucibles, and as it melts down more is added from time to time, the slag being poured off. The metal in the crucible is then submitted to the following refining process :—With the furnace tilted forward, the operator throws a handful of bone ash over the surface of the molten metal. This thickens whatever slag still remains, and enables it to be easily removed by means of spirals of 0·5-inch round iron. The air striking the exposed surface of the metal rapidly oxidizes the zinc and copper. After a couple of minutes, borax is thrown on, and dissolves the oxides, forming a slag which is thickened with bone ash and removed as before. After about two repetitions of this refining the precious metals are ready for pouring. The metal is then cast, yielding bars of bullion 850 to 900 in fineness.

Aluminium powder instead of zinc for the precipitation of silver from cyanide solutions is in successful use at Deloro, Ontario, and at the Nipissing Mine, Ontario. An account of the procedure at these mines is given by S. F. Kirkpatrick, for the former, in the *Engineering and Mining Journal*, 28th June, 1913, and for the latter, by E. M. Hamilton in the same journal, 10th May, 1913.

The following is a brief abstract of these important papers :—

At Nipissing it was found that when zinc was used as a precipitant the cyanide solution lost much of its dissolving power after the silver had been precipitated. This was traced to the presence of arsenic in association with the zinc which had passed into solution. Aluminium dust was substituted for zinc dust, and the trouble was removed.

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* *Eng. and Min. Journ.*, Sept. 1912, p. 597.

† *Eng. and Min. Journ.*, November, 1912.

The use of aluminium was proposed by Moldenhauer in 1893, but its first commercial application was made at the Deloro Mine in 1908.

The advantages possessed by aluminium as compared with zinc are—that it does not form any compound with cyanogen. and not only is the whole of the cyanide recovered which was combined with the precious metals, but the additional loss of cyanide by direct combination with the zinc is avoided.

As aluminium does not replace the precious metals in their cyanogen compound, the presence of a caustic alkali is necessary, the probable reactions being—

$$\text{Either } 6NaAgCy_2 + 6NaHO + 2Al = 6Ag + 12NaCy + 2Al(HO)_3,$$
$$\text{or } 2NaAgCy_2 + 4NaHO + 2Al = 2Ag + 4NaCy + Na_2Al_2O_4 + 4H.$$

The reaction when Zn is used being, according to Clennell—

$$NaAgCy_2 + 2NaCy + Zn + H_2O = Na_2ZnCy_4 + Ag + NaHO + H.$$

Caustic soda is added to the pulp before cyanide treatment, in sufficient quantity to bring the solution up to from 2 to 3 lbs. NaHO per ton. Lime must be reduced to the smallest quantity necessary for slime settlement, because it tends to form with the dissolved aluminium an insoluble calcium aluminate, which collects in the precipitate press, giving a low-grade product and one almost impossible to melt by the usual methods.

The amount of aluminium dust used at Deloro is slightly more than one-eighth of the silver present. At the Nipissing Mine the consumption of aluminium averages 0·02 lb. per oz. of silver.

Violent agitation is necessary as the dust is not readily wetted, and even when wetted it is difficult to get it to sink. This is effected at Deloro by using a tank having a vertical shaft in its centre carrying screw propellers, which when revolved agitate the solution and create a vortex, by which the dust is drawn down.

At Nipissing two small tanks are used, in which the solution and dust are very vigorously agitated by revolving stirrers.

In either case the precipitate is collected in a filter press.

The cakes at Nipissing are briquetted with soda and borax, and melted in a small oil-fired reverberatory yielding bullion over 997 fine.

As an alternative to the use of the dust, Charles Butters has proposed the use of aluminium granulations, which are cheaper than the dust, and to effect the precipitation in a tube mill, the attrition produced thereby serving to scour off any Al_2O_3 deposited on the surfaces of the metal, and thus keep them clean and active. As regards the cost of the precipitation by aluminium as compared with that by zinc, the advantage is in favour of aluminium.

Sodium sulphide has recently been used at the Nipissing mine as a precipitant for silver from cyanide solutions owing to the high price of aluminium dust and caustic soda.*

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* R. B. Watson, Bulletin, *Canadian Inst. Min. Eng.*, Nov. 1916.

The cyanide solution is agitated with solution of sodium sulphide in slight excess and pumped to a Merrill filter press. The required amount of sodium sulphide is ascertained by constant testing of the barren solution leaving the filter press. The solution from the filter press is aerated thoroughly in the barren-solution tank by air lift and a large circulating pump, the object being to oxidize any sodium sulphide that may be in slight excess in the precipitated solution, after which the regenerated cyanide liquor is returned to the treatment tank. The regeneration of cyanide by sodium sulphide is similar to that when aluminium is used for the precipitation of silver. The reaction is represented in the following equation :—

$$2NaAgCy_2 + Na_2S = Ag_2S + 4NaCy.$$

The silver sulphide precipitate is transferred to a tank and mixed with 4 parts of a solution containing 8 per cent. caustic soda (0·03 lb. NaOH per oz. Ag), a mechanical stirring device being employed. Above the tank is mounted a small tube mill charged with aluminium ingots weighing about 300 lbs., which fills the mill half-full. Through this mill, which makes 10 revolutions per minute, the pulp is circulated by means of a centrifugal pump. After 10 to 12 hours' desulphurization is complete according to the following equation :—

$$3Ag_2S+2Al+5NaOH = 6Ag + Na_2Al_2O_4 + 3NaHS + H_2O.$$

It is then pumped to a filter press, where it is washed for two hours, after which it is charged without drying to a reverberatory refining furnace for the removal of the sulphur, and melted down to a bullion which averages about 996 fine. The slag is saved and put through a small blast furnace.

The above process is limited in its application to silver ores, as gold sulphide is not precipitated in an alkaline cyanide solution. It is possible, however, when gold is present, that the process could be used to precipitate the silver and be followed by the precipitation of the gold by aluminium.

Treatment of Concentrates.—The concentrates always contain gold and, when treated at the cyanide plants, the methods described under "Gold," p. 352, are usually practised.

The work of the mills now to be described is typical of the best modern practice of cyaniding silver ores.

EXAMPLES OF PRACTICE.

San Rafael Mill, Pachuca.—An all-sliming mill. In Fig. 161 * is shown the arrangement of the plant.

The ore is broken in Blake rock breakers, crushed in a stamp battery (80 stamps), in cyanide solution, to pass through 10 to 12-mesh screens. The mill solution averages 0·25 per cent. of KCy, and 6 to 12 kilos. of lime are added to each ton of ore in the bins. The extraction during the crushing averages about 38 per cent. of silver and 70 per cent. of gold in the ore.

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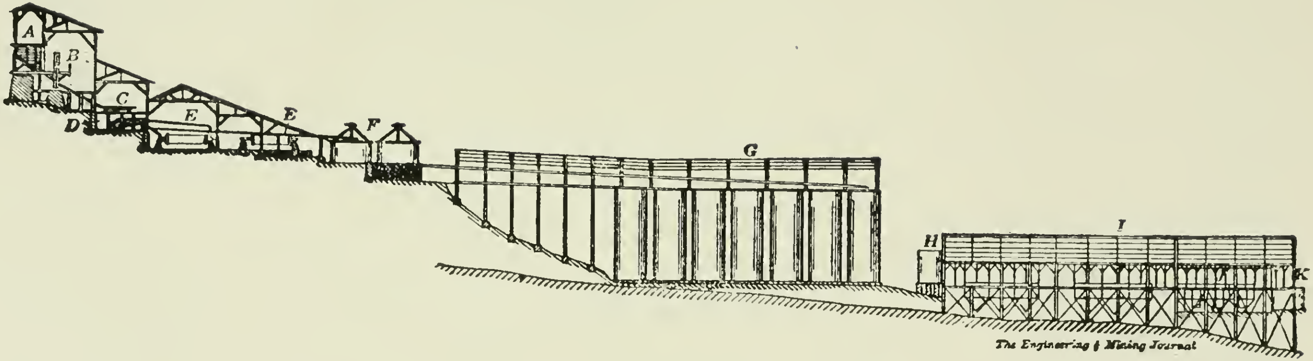
* *Eng. and Min. Journ.*, July, 1910 ; *ibid.*, February, 1913.



The Engineering & Mining Journal

A, Bins.
B, Stamps.
C, Wilfley Tables.
D, Dorr Classifiers.
E, Krupp Tube Mills.
F, Dorr Thickeners.
G, Pachuca Tanks.
H, Tanks for water from the Moore Filters.
I, Moore Filters.
J, Compressors and Pumps.
K, Tanks for storing Solutions.

Fig. 161.—San Rafael Cyanide Mill, Pachuca.

The pulp is distributed to sixteen Wilfley tables, and from them to five Dorr classifiers, the coarse going to five tube mills (4 feet by 20 feet), and the slime to five Dorr thickeners.

The tube-mill pulp passes to the classifiers, the coarse being returned, and the slimes going to the five Dorr thickeners. The thickened slime, consisting of 1 dry slime to 1·2 of solution, is treated in Brown vats (45 feet by 10 feet), of which there are ten. It is agitated in these vats for thirty-six hours with 0·3 per cent. KCy solution, then left to rest for twelve to twenty-four hours. The contents of the vats are led to Moore filters, from which the solutions flow to zinc boxes. The precipitate is pressed, and melted in crucibles with fluxes, the resulting bullion averaging 920 to 950 silver and about 8·3 gold per thousand. The ore before treatment contained about 30 ozs. silver and 3 dwts. gold per ton, and the extraction was 91·4 per cent. of the silver and 97 per cent. of the gold, as mentioned above.

*Montana-Tonopah Stamp and Cyanide Mill, Nevada.**—An "all-sliming" plant with double concentration. Trent and Hendryx agitators and heated solutions are employed. The flow sheet in 1912 is shown in Fig. 162.

The ore carries about 20 ozs. silver and about 4 dwts. gold per ton. The total extraction is 92·6 per cent.

"The ore is broken in Gates breakers, to pass through a 2-inch ring. The product goes to other breakers of the same type, to pass a $\frac{3}{4}$-inch ring, and then to the stamps, where it is crushed through 16-mesh screens.

"There are forty stamps, weighing about 1,050 lbs. each. The pulp from each five-stamp battery is delivered to a cone classifier. The spigot or coarse product of each is delivered to a Wilfley concentrating table, of which there are eight in all, and the overflow from each cone is delivered to two Dorr classifiers. The tailing from the Wilfley tables is also delivered to the Dorr classifiers.

"In the Dorr classifiers a separation of the sand and slime is made. It is aimed to crush all the pulp to 150 mesh and finer in the tube mills; these classifiers separate that part of the pulp which is already crushed to this size, and it is delivered to the thickening cones for dewatering.

"The coarse sand product from the Dorr classifiers is delivered into two 5 by 22-foot tube mills. The sands are all ground to 150 mesh, or finer in these mills, and each mill discharges its product into a classifying cone 4 feet in diameter. These cones are for the purpose of separating any sands from the product which might have passed through the mill, without being reground fine enough, and these sands are elevated back to the Dorr classifiers, to be fed again to the tube mills. This is called the closed-circuit system.

"The finished product is delivered to sand pumps, by which it is elevated to two large settling or pulp-thickening cones, where the excess of water is removed. The thickened pulp from the bottom discharge is delivered to sixteen Frue vanning machines. These concentrators remove and collect any fine sulphides after regrinding, in addition to that saved by the Wilfley tables. All the concentrate is collected and dried, after which it is shipped to the smelters.

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* *Eng. and Min. Journ.*, May, 1908.

"The tailing from the vanners and the overflow from the settling cones are delivered as a slime to any one of three dewatering or settling tanks. These tanks are provided with filters, through which the water is drawn off and flows to a final settling box to collect any slime carried in suspension.

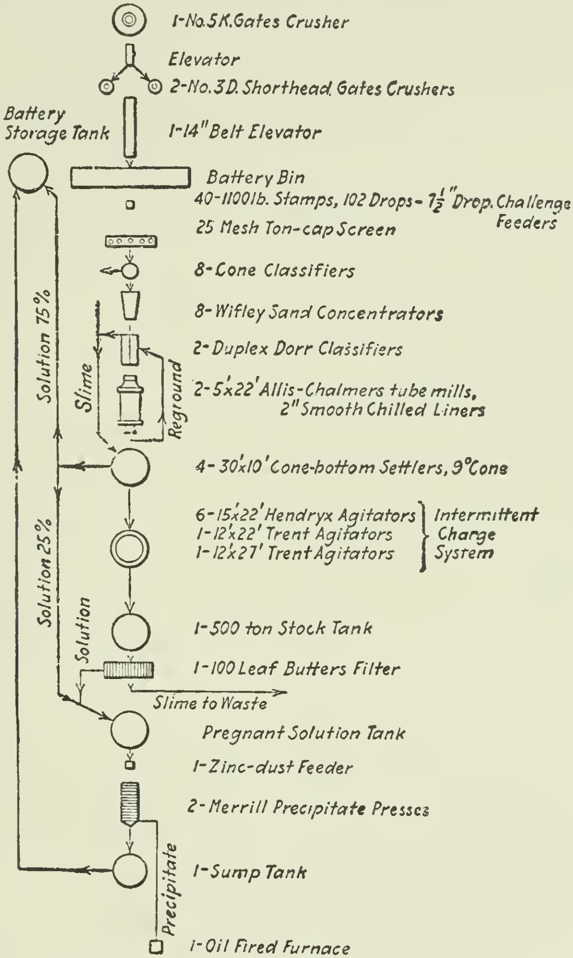
1-No.5K.Gates Crusher
Elevator
2-No.3D.Shorthead Gates Crushers
Battery Storage Tank
1-14" Belt Elevator
Battery Bin
40-1100lb. Stamps, 102 Drops-7½" Drop. Challenge Feeders
25 Mesh Ton-cap Screen
8-Cone Classifiers
8-Wifley Sand Concentrators
2-Duplex Dorr Classifiers
2-5'x22' Allis-Chalmers tube mills, 2" Smooth Chilled Liners
Solution 75%
Slime
Reground
4-30'x10' Cone-bottom Settlers, 9° Cone
6-15'x22' Hendryx Agitators
1-12'x22' Trent Agitators
1-12'x27' Trent Agitators
Intermittent Charge System
Solution 25%
Solution
1-500 ton Stock Tank
1-100 Leaf Butters Filter
Slime to Waste
Pregnant Solution Tank
1-Zinc-dust Feeder
2-Merrill Precipitate Presses
1-Sump Tank
Precipitate
1-Oil Fired Furnace

Fig. 162.—Flow Sheet, Montana-Tonopah Mill, 1912.

"The thickened and dewatered pulp from the settling tanks is drawn off from the bottom discharge through a pipe line connected to the suction of a 6-inch centrifugal pump.

"The pulp is delivered by the pump into the agitator tanks. There are six agitators of the Hendryx type, and two of the Trent type. The agitation is continued for from 30 to 54 hours in a solution containing 5 lbs KCy per ton. Lime is added to the agitators about 3 lbs. for each ton of ore. The solutions are kept heated to about 110° F. (43·3° C.).

"After the required period of agitation, the pulp is drawn from these tanks by a centrifugal pump, and is delivered into the pulp-storage tank. This tank is provided with a stirring gear, which keeps the pulp in gentle agitation to prevent settling. From this tank the charges are drawn into the filter boxes of the Butters vacuum system, and the solutions leaving the boxes are precipitated by zinc dust in two Merrill precipitation presses."

The practice of using hot solutions at Tonopah is briefly as follows:—*

At the new Belmont Mill, the temperature at the stamps is from 60° to 70° F. (15·5° to 21·1° C.), and at the Brown agitators exhaust steam, from the mill air compressor, is fed in, increasing it from 90° to 100° F. (32·2° to 37·8° C.).

At the Montana-Tonopah, ore is crushed in 50° to 60° F. (10° to 15·5° C.) solution, which is increased to 110° F. (43·3° C.) at the Hendryx agitators by live steam.

It is found also that the heat aids settling. There is a marked decrease in extraction without hot solutions.

The Extension ore is crushed in 80° F. (26·6° C.) solution, and live steam is added to the Trent agitators, as soon as possible, making the temperature up to 120° F. (49° C.).

It was found that this was better than 90° F. (32·2° C.), and extraction has improved 1·5 to 2 per cent. during the past few months, it being 94·5 per cent. at present.

At another plant treating Tonopah ore, crushing is done in 76° to 80° F. (24·4° to 26·6° C.) solution, increased to 95° F. (35° C.) in the agitators by live steam in coils. Recent tests showed a saving of 24 to 32 cents at a cost of 11 cents per ton.

In the Tonopah district it is the universal opinion that the extraction of silver is increased by heating the cyanide solutions.

Continuous Cyaniding in Brown or Pachuca Vats.—By this method the first of a series of vats is charged with pulp, from which it is led by suitable connecting pipes to a second, and thence successively to the remaining vats of the series.

A good example of the method, as carried out in practice, is afforded by the Esperanza Mill at El Oro (Mexico).†

The vats are 45 feet high and 15 feet in diameter. There are six in the series, and they are connected by 6-inch pipes (Fig. 163).

These pipes are so arranged that the inlet of each is 5 feet 6 inches below the top of the central column, and 2 feet distant from it, the delivery being about 3 feet below the top of the conical bottom of the adjoining vat, and midway between the side of the vat and the central column.

The discharge from the last vat passes to a storage tank, 30 feet diameter

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* *Min. and Sc. Press*, Dec. 1912.

† *Mexican Min. Journ.*, August, 1910.

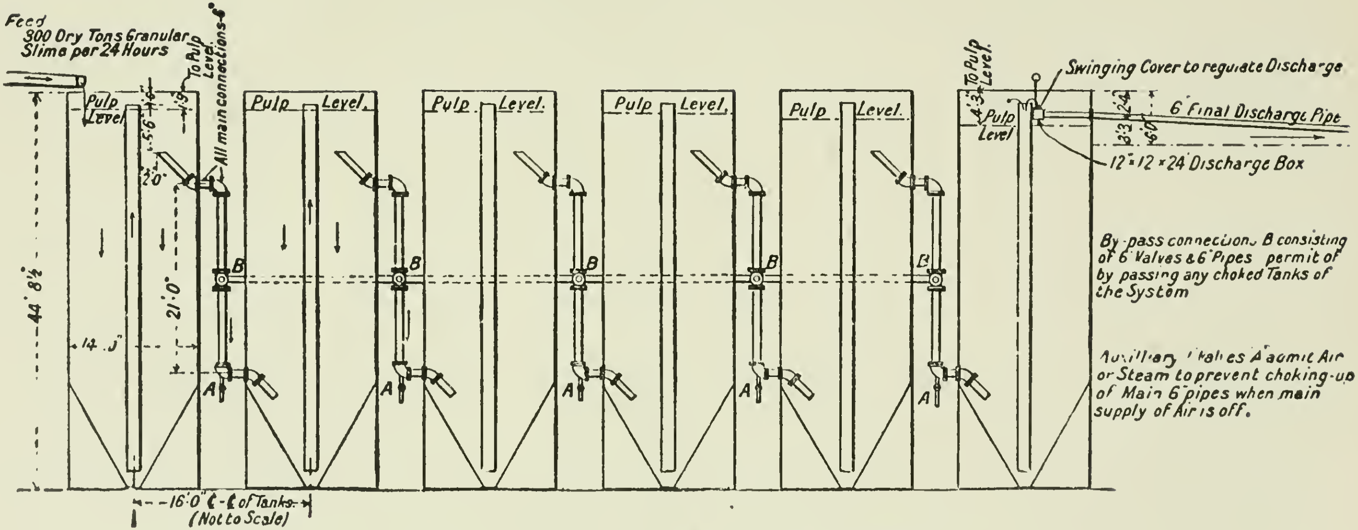
Feed
300 Dry Tons Granular Slime per 24 Hours
Pulp Level
To Pulp Level.
All main connections 6"
1'6"
5'6"
2'0"
21'0"
14'0"
44'8½"
16'0" ℄-℄ of Tanks (Not to Scale)
Pulp Level.
B
A
To Pulp Level.
4'3"
Swinging Cover to regulate Discharge
2'4"
3'3"
6'0"
6" Final Discharge Pipe
12"×12"×24" Discharge Box
By-pass connection B consisting of 6" Valves & 6" Pipes permit of by passing any choked Tanks of the System
Auxiliary Valves A admit Air or Steam to prevent choking-up of Main 6" pipes when main supply of Air is off.

Fig. 163.—Brown Vats arranged for Continuous Cyaniding

by 12 feet deep, in which it is kept in agitation by a mechanical stirrer, and thence to Merrill filter presses. The solutions from the filter presses are pumped through Merrill precipitation presses with zinc dust. The gain in the extraction with the continuous system, as compared with the intermittent, is 1·3 per cent. of gold and 1·5 per cent. of silver, and the saving in cyanide 25 grammes per ton of ore treated.

*Santa Gertrudis Mill, Mexico.**—The ore from the gyratory crushers passes to the battery bins, from which it is fed to sixty 1,550-lb. stamps with 3-mesh and 4-mesh screens, where it is crushed in mill solution. Sodium cyanide is used, and the strength of this mill solution is equivalent to 0·4 per cent. KCN. The pulp from the batteries flows through split distributing launders to six primary duplex Dorr classifiers, the sand passing to six 5- by 16-foot tube mills, the discharges from which are delivered to the secondary classifiers by an elevator or Frenier pumps. The slime which overflows from the primary classifiers is laundered to eight secondary Duplex Dorr classifiers, which feed the sand to four 5- by 20-foot and two 5- by 22-foot tube mills, the discharges from which are returned to the classifiers. The slime which overflows from the secondary classifiers passes to six primary Dorr thickening vats, 35 feet diameter by 15 feet deep, wherein the pulp is thickened from 10 : 1 to 1·5 : 1.

The thickened pulp is delivered to a set of fourteen primary Brown agitators, 15 by 45 feet, operating in series; the discharge from the last agitator in the series is delivered to a launder, where a wash of 4 parts of mill solution is applied, the pulp flowing to four secondary Dorr thickening vats, wherein it is again thickened to about 1·75 : 1. It is then delivered to a set of fourteen secondary Brown agitators, also operating in series, the discharge from the last agitator flowing to two 35- by 12-foot storage tanks equipped with mechanical stirrers. These storage tanks feed by gravity, at 35 lbs. pressure, four Merrill filter presses. The pregnant solution from the presses is clarified by passing through four sand-filter vats.

Protective alkalinity is maintained at about 0·75 per cent., the lime being fed dry into the ore at the crushing plant.

Crude litharge is used in place of lead acetate. It is ground in a small tube mill, 24 inches diameter by 37 inches long, and is charged into the first Brown agitator at the rate of 0·6 lb. per ton of ore.

Precipitation is effected by the Merrill zinc-dust process. Two circuits are maintained, one precipitating to barren solution, sufficient for the filter-press washing, and the other circuit to an effluent containing from 0·9 to 1·2 oz. silver per ton. The precipitate is dried by blowing air through the presses at 25 lbs. pressure until it contains only about 30 per cent. moisture. The precipitate is then removed from the presses and melted without further drying in a battery of eight oil-fired crucible furnaces, arranged on the arc of a circle, and served by a radial jib-crane fitted with an air cylinder for raising and lowering the pots. The precipitate is charged into the crucibles, a flux of 1½ per cent. each of borax and bottle-glass being added on the top without mixing, and when melted is skimmed and cast into bars. As the bars are poured, sticks of wood are laid on top, which ignite and prevent too rapid cooling of the centre of the bar, thus subsidence and holing are avoided. The bars weigh 1,000 ozs. each, and assay 5·0 gold and 950 silver fine.

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* *Min. and Sc. Press*, August, 1916. (Abstract of a paper by Hugh Rose read at a meeting of the A.I.M.E.)

The mill is electrically driven throughout, 50-cycle alternating current being distributed at 440 volts.

*The Nevada Packard Mill, Humboldt County.**—This mill, which was erected in 1915, is an excellent example of the most recent practice in the cyaniding of silver ores.

It is an all-sliming plant with a typical equipment of the continuous counter-current-decantation system. The ratio of gold to silver in the ore is about 1 : 300, the silver mineral being kerargyrite. The ore is crushed in gyratory crushers, when a small amount of lime is added to give the necessary alkalinity. It is further reduced to $\frac{3}{8}$ of an inch by rolls, and then fed into No. 1 tube mill (6 feet diameter and 5 feet long), where the ore first comes in contact with the cyanide solution, sufficient being added from the stock tank to bring the moisture content up to 40 per cent.

The pulp from the tube mill flows to a Dorr duplex classifier, the discharge from which passes to the second tube mill (6 feet diameter by 10 feet long), the pulp from which is again returned to the classifier until it is ground to 200 mesh.

Selected lumps of the ore have largely replaced Danish pebbles in the tube mills.

The overflow from the classifier, diluted to about 7 : 1, is elevated by a Frenier pump to No. 1 Dorr thickener (28 by 10 feet). The solution from the thickener overflows to a clarifying vat in which sixteen Butters canvas leaves are suspended. The clear solution is drawn through these leaves by a rotary pump, and discharged into the pregnant solution tank. From this tank the solution is pumped through one or two Merrill precipitation presses, the two presses being used alternately.

The pregnant solution has averaged $1·37 and the barren effluent 7 cents. By testing the effluent frequently, with 10 per cent. sodium sulphide solution, the mill men keep the silver content within a few cents of the latter figure. This method of testing the effluent is in use in many cyanide plants treating silver ores, yet it does not seem to be generally known.

Returning to the mill circuit, the underflow from No. 1 thickener is discharged into the first of two Dorr agitators, each 28 by 16 feet, where it is diluted with stock solution. The lead acetate and most of the cyanide are added in this agitator, the remainder being dissolved in the stock tank. The cyanide strength is kept about 2 lbs. KCN, and the protective alkalinity at 0·8 lb. CaO per ton.

The two agitators are connected in series by a straight pipe.

From the agitators the pulp flows by gravity to the feed-box of No. 2 Dorr thickener, the first of two decantation vats. It is diluted in the box by the overflow from No. 3 thickener. The clear solution flows to the sump tank. The discharge is transferred by a diaphragm pump to No. 3 thickener, where it is diluted with the barren solution discharged from the Merrill presses. The underflow is discharged into an Oliver filter.

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* H. G. Thomson, *Min. and Sc. Press*, Sept. 1916.

In this system it will be seen that barren solution is taken in at the final thickener, and passed back until it overflows at the first thickener, being thereby enriched and the pulp impoverished.

The extraction is 94·9 per cent. of the Ag and Au in the ore.

Treatment of Silver Ores at Cobalt, Ontario.—The silver occurs in stringers, largely as native silver, in a calcite gangue, associated with sulphide and antimonial sulphide of silver, and arsenides and sulphides of nickel and cobalt. Some of the deposits are of extraordinary richness; thus a shipment of the Temiskaming Mining Company, in December, 1911, of about 30 tons; contained 200,337 ozs. of silver, and another in February, 1912, of about 25 tons, contained 202,806 ozs. A typical high-grade ore contains Ag 10 per cent., Co 9 per cent., Ni 6 per cent.; and As 39 per cent., the remainder is CaO, SiO_2, and smaller amounts of Sb, Fe, S, Te, etc.

Nipissing Mining Company.—At the High-Grade Mill it was treated by a combination of amalgamation and cyaniding, as follows :—*

The high-grade ore, from the picking table, after being crushed in a ball-mill, is fed into a Krupp tube mill, 19 feet 8 inches long by 3 feet 11 inches in diameter, with a silex lining. The ore contains about 2,500 ozs. silver per ton. The charge consists of ore 3½ tons, mercury 4½ tons, pebbles 6 tons, and about 2 tons of cyanide solution containing 5 per cent. KCy. The mercury used is about fifteen times the weight of silver in the ore, as it is necessary to keep the amalgam very thin, otherwise it would stick in the tube mill and cake under the shoes of the settler.

The ends of the tube mill are closed, and compressed air, under 25 lbs. pressure, is forced in during the revolution of the mill.

The mill is revolved for 9½ hours, when 97 to 98 per cent. of the silver will have been extracted by the mercury, and 99 per cent. of the pulp will pass a 200-mesh screen.

The charge is then transferred to a settler, 8 feet in diameter, with wooden shoes, where the amalgam is separated, and thence goes to a clean-up pan. The cleaned amalgam is strained in canvas bags, to remove excess of mercury, and is then retorted in cast-iron retorts, 14 inches by 60 inches, set in pairs in furnaces fired by oil.

The sponge from the retorts is charged into an oil-fired reverberatory furnace, with a magnesite hearth, in charges containing 28,000 ozs. of silver, and kept molten for about 18 to 20 hours, its surface being exposed to a blast of heated air to oxidize the impurities which are present. No fluxes are used. As soon as dip samples assay 999 fine the silver is tapped and cast into ingots. No less than 20 tons of mercury are in use at a given time. The cyanide has a cleansing action upon it; indeed, the use of mercury would be impracticable without the cyanide, for the mercury would become "sick" or fouled, so as to hinder amalgamation with the silver in the finely ground arsenical ore.

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* *Eng. and Min. Journ.*, Dec. 1912, and *Min. Mag.*, vol. vi., p. 452.

The cyanide treatment of the pulp is comparatively unimportant, as it deals only with 6 or 7 tons of 50-oz. ore daily. A charge for agitation is made up of four tube mill charges of 13 tons of dry pulp. Five pounds of lime per dry ton of pulp are added and the charge is agitated for thirty-six hours.

The vats, 16 feet by 7 feet, are fitted with mechanical agitators, and the pulp is circulated through a pump as well. The cyanide strength is 0·75 per cent.

After settling, the solution is decanted, and the pulp is run to a Butters filter of ten leaves. To avoid the settling of the heavy pulp in the bottom of the filter box while the cake is forming, the charge is kept in circulation by an air lift drawing out of the bottom of the box and delivering at the top. The cake is washed 2½ hours with weak solution, and then discharged.

There are two zinc precipitation boxes, one for strong and one for weak solution. The precipitate from both boxes goes to an 18-inch Johnson filter press ; the press holds 500 lbs. of precipitate, which assays 15,000 ozs. silver per ton.

In 1913 precipitation by aluminium dust was adopted and precipitation by zinc abandoned.

The above process was worked satisfactorily for seven years, but, owing to war conditions having greatly increased the price of mercury, it was decided to discontinue amalgamation and to adopt cyaniding after giving the ore a preliminary treatment with bleaching powder in the tube mill. The new process, which was devised by Mr. M. F. Fairlie, is as follows :—*

" The low-grade ore is concentrated in the usual way on tables, the slime going direct to a cyanide annexe. The table concentrate is reconcentrated on tables and brought up to 2,000 ozs., while the tailing from this treatment is sent to the cyanide plant with the slime. The rich concentrate, together with the high-grade ore, is then ground wet for 24 hours in a tube mill equipped with iron linings and balls. To this charge is added, towards the end of the operation, 2 per cent. bleaching powder. The effect of the bleaching powder is to oxidize the refractory silver minerals and make them amenable to treatment by cyanide. The charge from the tube mill goes to a Dorr classifier, where the coarse material, including the metallics from the ore, is removed. The pulp, after being well washed, is dewatered by an Oliver filter and treated by a strong cyanide solution. The final residue, after filtration on another Oliver filter, can be readily marketed for its cobalt and silver content.

" The silver-bearing solution is precipitated by sodium sulphide, the resulting precipitate being desulphurized in a small tube mill by the aid of metallic aluminium and a caustic soda solution (see p. 402). The over-size raked out by the classifier is given a partial roast on the hearth of a furnace, to eliminate part of the arsenic, and is then melted down to bullion. The small amount of speise and slag is returned to the tube mill with the next charge."

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* R. B. Watson, *Canadian Mining Journal*, March, 1917.

The Deloro Reduction Company, Cobalt, Ontario.*—The material treated consists of high and low-grade silver-cobalt ore in lump form, jig and table concentrate, and ore residues. The ore is smelted in a blast furnace, the charge being calculated so as to furnish a practically neutral slag, and on account of the large quantity of fines present, the furnace is run generally at a blast pressure of only 6 to 8 ozs. The ore and returns from other sections of the plant are mixed wet and charged to the furnace in the form of a stiff mortar, which sinters fairly well before the smelting zone is reached. The products of the smelting operation are speise, from which a quantity of base silver is liquated in the case of high-grade runs; slag, and arsenic fume.

The speise contains approximately, Co 22 to 25 per cent., Ni 16 to 18 per cent., As 25 per cent., Fe 18 per cent., S 7 per cent., Cu 1 per cent., Ag 1,000 to 1,200 ozs. per ton.

The speise is first liquated to recover part of the silver, then ground to pass a screen with 40 meshes to the inch. The ground material is then roasted in a reverberatory furnace equipped with mechanical rabbles until it contains only 10 per cent. As. It is then subjected to a chloridizing roasting in a Brückner cylinder. The chloridized speise is washed with water and then agitated for one hour with a cyanide solution containing the equivalent of 20 lbs. KCN per ton. The silver is precipitated from the solutions with aluminium dust, the cyanide being almost quantitatively regenerated. The precipitate is sent to the silver refinery, and the desilverized speise residue to the oxide plant. In the silver refinery the crude silver liquated from the speise is refined by melting it in an oil-fired furnace in the form of a small converter, and blowing air through it for about three hours. When finished the charge is poured into ingot moulds. The silver bullion thus obtained averages from 992 to 995 fine, and is brought up to commercial grade (996 and better) by remelting with silver precipitate from the cyanide plant. The gases from these operations are drawn through coolers and passed to a small bag-house.

The gases from the blast furnace, the roasters, and chloridizers are drawn through flues and coolers before reaching the bag-houses, which collect the crude arsenious oxide. This is sent to refining furnaces, which are coke-fired reverberatory hearths. The pure arsenious oxide being collected in condensing chambers. The clinker or slag from these hearths contains all the silver that was formerly present in the crude arsenic and goes back to the blast furnace.

The desilverized speise residues which contain the cobalt and nickel content of the ore chiefly in the form of oxides is sulphatized, to render the cobalt and nickel soluble as sulphates. The sulphatized speise is leached with hot water, and the liquors thus obtained are first freed from copper and iron (see p. 548). The cobalt is then precipitated with hypochlorite solution, and the nickel after removal of the cobalt, with milk of lime. The hydroxides of cobalt and nickel thus obtained are filter-pressed, crushed, and dried, and powdered for sale, or are transferred to the metals department for reduction to the metallic state. For the purpose of reduction the oxides are mixed with charcoal and reduced to crude metal in oil-fired furnaces. After separation from excess of carbon by means of a magnetic separator the crude metal is remelted in electric furnaces and granulated by pouring into water.

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* Sydney B. Wright, Abstract from Bulletin 80, *Canadian Min. Inst.*, 1918, pp. 992 to 995

The flotation process has been introduced during recent years in several plants at Cobalt. It has not, however, replaced the old systems of water concentration, but has been found to be of service for saving the finely ground particles of argentite, pyrargerite, and other silver minerals in the tailings from the concentrating tables.

The other wet processes, the Augustin, Patera, Russell, and Ziervogel, are either obsolete in most silver extraction works, or are rapidly becoming so. For the first three processes, the silver must be in the state of chloride, hence the ore to be treated by them must first be subjected to a chloridizing roast, as described on p. 390.

The last, the Ziervogel process, is only applied to the extraction of silver from mattes.

(3) **The Augustin Process.**—The process is only in use at a few places, and on a small scale, but was formerly largely employed for the extraction of silver both from ores and argentiferous copper matte.

In the treatment of ore, it consists of the following operations:—

1. Chloridizing-roasting.

2. Leaching the chloridized ore with hot solutions of common salt in wooden vats.

3. Precipitation of silver from the solution from the leaching vats by means of copper.

4. Washing, purifying, and casting the silver into ingots.

5. Recovery of the copper from the liquors from the precipitation tanks by means of iron.

6. Melting and refining the copper to be used again.

When copper matte was treated there was an additional operation—viz., the recovery of the copper from the residue in the leaching vats by smelting and refining.

One of the most successful plants was formerly at work at Kosaka, Japan. The ore contained only 11½ ozs. silver per ton, with 49·5 per cent. barytes, and a little zinc blende and iron pyrites, but was treated with profit. The procedure was as follows:—The ore was first roasted with common salt. The lixiviation vats were of wood, twenty-one in number, and elliptical in shape, their dimensions being 7 feet long, 5 feet wide, and 2 feet 6 inches deep, and the capacity of each 2 tons of roasted ore. The false bottom was a wooden grating with 1-inch holes, and the filter cloth two sheets of straw matting. The vats were filled with ore, and hot brine, containing 18 per cent. of common salt by weight, was run on from the storage tank by means of a launder which ran the whole length of the row. The leaching was continued until a polished plate of copper held at the discharge tap showed no trace of silver. The flow of brine was then cut off, and the liquor from the leaching vats turned away from the precipitation vats into the brine sump. The brine in the tailing was then washed out by a stream of warm water. The leaching occupied about ten to twelve hours. The tailing was thrown away.

The precipitation vats were of brick, lined with cement. They were 125 feet long, and were divided into eight compartments, to facilitate "cleaning-up." The vats were set in two rows, an upper and a lower, in front of the leaching vats.

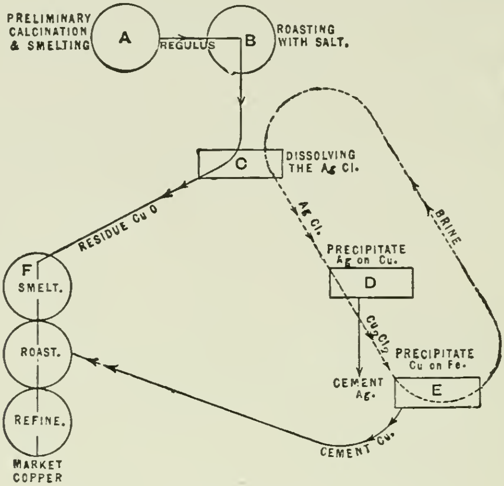
PRELIMINARY
CALCINATION
& SMELTING
A
REGULUS
B
ROASTING
WITH SALT.
C
DISSOLVING
THE Ag Cl.
RESIDUE Cu O
Ag Cl.
BRINE
PRECIPITATE
Ag on Cu.
D
F
SMELT.
ROAST.
REFINE.
MARKET
COPPER
Cu₂Cl₂
PRECIPITATE
Cu on Fe.
CEMENT
Ag.
E
CEMENT Cu.

Fig. 164.—Flow Sheet. Augustin Process.*

The upper vats served only to settle out fine ore slimes and basic salts of iron in the liquors. The silver vats were provided with false bottoms, like those of the leaching vats, and over which a 2-inch bed of bean-shot copper was spread to form a filter bottom. Upon this bed rested a number of "tiles" of copper, 8 inches by 6 inches by $\frac{1}{2}$ inch, bent like ridge roofing tiles and laid similarly. The lowest tank was filled with scrap iron for precipitating the copper. This copper was melted, refined, and used again.

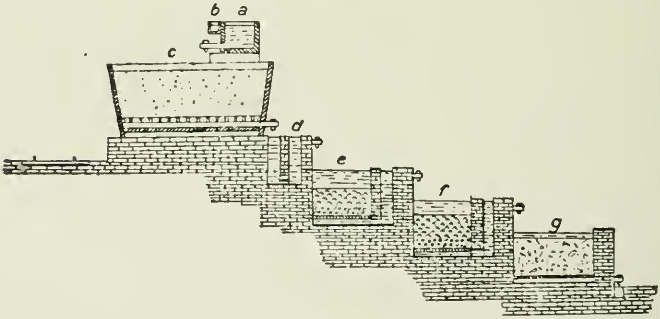

Fig. 165—Augustin Process, Leaching and Precipitation Vats.†

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* Roberts Austen, *Introduction to Metallurgy*, p. 428

† Collins, *Silver*, p. 176

The cement silver was refined as follows :—After being washed, it was squeezed by a screw press into discs 1 foot diameter by 3½ inches thick. The discs were dried, and refined in charges of 125 to 170 lbs. in English cupellation furnaces, 300 lbs. of lead being added to each charge. The refined silver was remelted in plumbago crucibles, and cast into bars of 1,000 ozs. each, which averaged 985 fine.

In Fig. 164 is given the "flow sheet" of the process, both for the treatment of ore and matte, and in Fig. 165 the arrangement of the plant at Kosaka.

(4) **Patera Process.**—This process is based on the solubility of silver chloride in solution of sodium thiosulphate (hyposulphite), and its precipitation from the solution by sodium sulphide, in accordance with the following reactions :—

$$2AgCl + 2Na_2S_2O_3 = Na_2S_2O_3, Ag_2S_2O_3 + 2NaCl$$
$$Ag_2S_2O_3, Na_2S_2O_3 + Na_2S = Ag_2S + 2Na_2S_2O_3$$

The method was first suggested by Dr. Percy, but it was first carried out on a practical scale by von Patera at Joachimsthal (Bohemia)

The ore to be treated by the Patera process should not contain much copper, or lead, or much calcite if sulphides are not present. The two former are converted into chlorides in the chloridizing-roasting, and are liable to be precipitated along with the silver, giving low-grade bullion. This is especially the case with lead, as the lead chloride is only partially removed in the water wash. Caustic lime tends to decompose silver chloride on the cooling floor after chloridizing-roasting. Arsenic and antimony do not interfere, as arsenates and antimonates of silver are soluble in the hyposulphite solution. Gold is but slowly and sparingly soluble in hyposulphite solutions, and the process is hence unsuitable for gold ores proper

The process consists of the following operations :—

1. Chloridizing-roasting of the ore as described, p. 390.
2. Leaching the chloridized ore with water to remove base metals. Some silver chloride is also dissolved, and has to be recovered (base metal leaching).
3. Leaching with solutions of sodium hyposulphite (silver leaching).
4. Precipitation of silver by sodium sulphide.
5. Conversion of the impure silver sulphide into silver bullion.

An excellent form of leaching vat is that designed by Russell for the process which bears his name. It is shown in plan and section in Fig. 166.

In large works the vats are usually 16 to 17 feet in diameter, 5 feet in depth if the tailing is shovelled out, and 7 feet if it is removed by sluicing. According to Hofmann, the best depth for leaching vats is 3½ to 4 feet Both staves and bottom should be from 3 to 4 inches thick, according to the size of the vats.

The false bottom for the filter consists of wooden slats, 1½ inches high, 1 inch wide, and 1 inch apart crossing at right angles and resting on the bottom of the vat. A clear space of about 1½ inches is left between the ends of the slats and the side of the vat. The filter consists of one thickness of cocoa matting, which just covers the slats, but not the annular space, and one thickness of canvas duck, which has been cut 6 inches larger in diameter than the vat. The latter is fastened down in the annular groove by driving in a ½-inch rope.

The hoops of the vat are 1⅛-inch round iron.

Each vat has an outlet for solutions in the centre of the bottom, to which a hose leading to the launders in front is attached, and also a lower hose, which connects with a Korting ejector, and with an upright pipe A. By this arrangement it will be seen that leaching can take place at the ordinary rate through the first-mentioned hose, or, by using the other hose and the

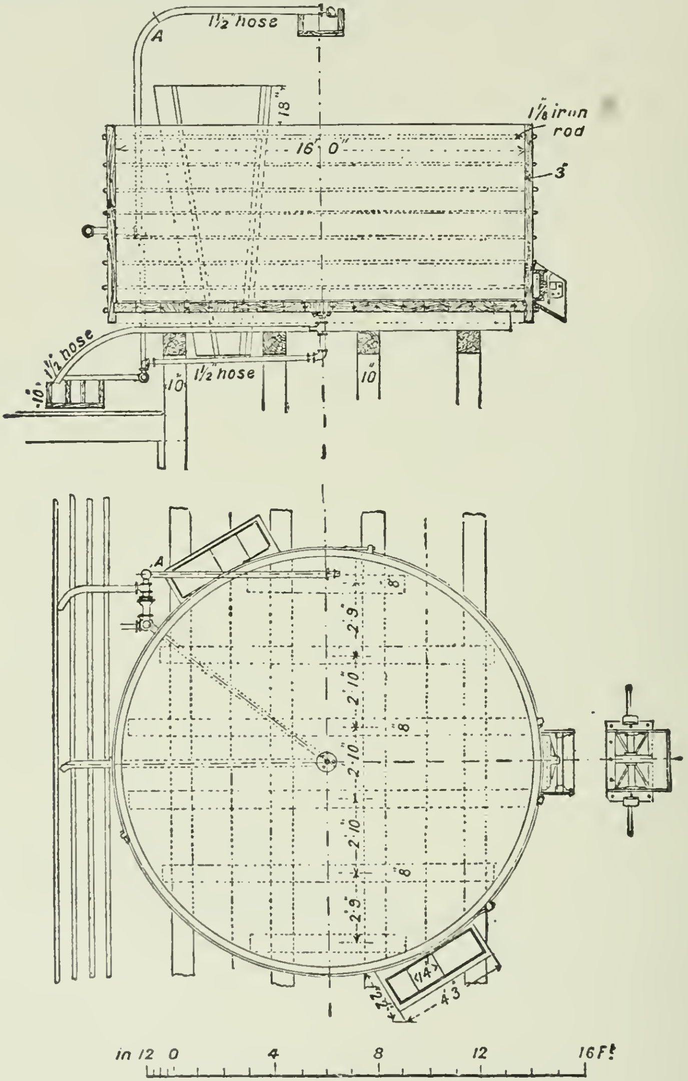
1½" hose
A
18"
1⅛" iron rod
16' 0"
3"
1½" hose
10"
1½" hose
10"
10"
A
8"
2' 9"
2' 10"
8"
2' 10"
2' 10"
8"
2' 9"
14"
4' 3"
2' 2"
in 12 0 4 8 12 16 Ft.

Fig. 166.—Leaching Vat.*

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* Stetefeldt, *The Lixiviation of Silver Ores*, p. 116

Korting ejector, it may be hastened, or the solution may be returned to the top of the vat if circulation is desired.

The triple launder in front serves for conducting the liquors, either to the wash-water vat or the precipitating vat, or to waste.

The precipitating vats are smaller and deeper than the leaching vats, and are usually about 10 feet in diameter and 8 to 9 feet in depth, or, if mechanical agitators are used, about 8 to 9 feet in diameter and 6 feet in depth.

The process is carried on as follows :—

Base Metal Leaching.—The chloridized ore is charged into the leaching vats, and is washed with hot water until the soluble salts of the base metals are removed. They are chiefly iron, copper, and lead chlorides, but owing to the common salt present some silver is also dissolved.

In order to minimise the solution of silver, Hofmann recommends * that the water be passed into the vat below the filter, until it rises above the ore. Thus the most concentrated portion of the solution will appear above the ore, and if then diluted with a stream of water and the course of filtration reversed a large part of the silver chloride will be precipitated and remain in the ore, while the outflowing solution will be dilute, although not sufficiently so as to be entirely free of silver.

The solution of the base metals is first run into a vat containing cement copper to precipitate the silver, and thence into another vat containing scrap iron to precipitate the copper.

Frequently the greater part of the silver is first precipitated by fractional precipitation by sodium sulphide, and only the remainder by copper.

Silver Leaching.—After the ore has been thus freed from the salts of the base metals, a cold weak solution of sodium hyposulphite is introduced on the top of the ore. According to Hofmann, the best strength of the solution is 0·25 to 0·5 per cent. of hyposulphite, as a weak solution dissolves silver chloride in preference to lead chloride.

At some works solutions containing from 0·5 to 1·0 or more per cent. are in use, but lead sulphate and cuprous chloride dissolve more readily in a strong than in a weak solution, and a low-grade bullion will result.

Gold as well as silver is dissolved by the hyposulphite solutions.

The leaching is continued until the escaping solution contains no silver, as shown by testing with sodium sulphide, or by other tests. The hyposulphite solution remaining in the ore is then displaced by a water wash.

Precipitation of the Silver.—The solution containing the silver is agitated vigorously in the precipitation vats, either by mechanical stirrers driven by bevel gearing, or by compressed air in large works, or in small establishments by hand paddles, a strong solution of sodium sulphide being carefully added, an excess being avoided. The silver is precipitated in accordance with the reactions given above, from which it will be seen that by the action of sodium sulphide, sodium hyposulphite is regenerated, and the solution is available for use in the leaching of other charges of ore.

Calcium polysulphide (CaS_5) has been proposed as a precipitant instead of sodium sulphide, but the advantages of its use have not been established. The reactions when it is used are—

$$Ag_2S_2O_3, Na_2S_2O_3 + CaS_5 = Ag_2S + CaS_2O_3, Na_2S_2O_3 + 4S.$$

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* Hofmann, *Hydrometallurgy of Silver*, p. 162.

Any lead, copper, tin, or gold in the solution will be precipitated together with the silver.

After the precipitate has completely settled, the clear solution is drawn off by a hose, the upper end of which is kept just below the surface of the liquor by a float, as shown in Fig. 167.

The precipitate is discharged into a storage vat, whence it is transferred to a filter press, in which it is well washed. It is then carefully dried in a small reverberatory furnace at a very low temperature, and then further heated to expel sulphur.

The precipitate, after drying, usually contains copper, often 14 to 25 per cent., silver up to 30 to 40 per cent., and sulphur about 20 per cent.

The product from the reverberatory furnace is either sold to smelting works, and this is generally the case, or it is treated by scorification on a bath of molten lead in an English cupellation furnace.

The extraction of silver by the Patera process when properly conducted may reach 90 per cent. of that contained in the ore, but it is sometimes only 70 per cent. or less.

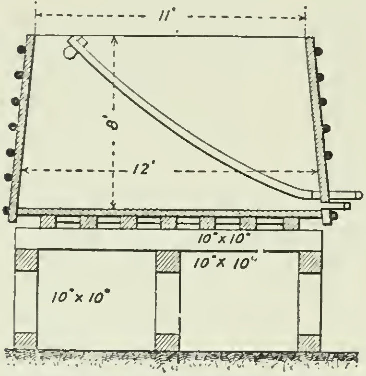

Fig. 167.— Precipitation Vat

(5) **The Kiss Process.**—In this process calcium hyposulphite was used for leaching the ore, and calcium polysulphide for the precipitation of the dissolved silver. It was claimed that the calcium salt was a more efficient solvent for gold than the sodium salt, but this has not been proved.

(7) **The Russell Process.**—The special feature of the Russell process is the use of a solution of cuprous sodium hyposulphite in addition to the ordinary sodium hyposulphite of the Patera process

This solution is called the "extra" solution, and is prepared by mixing 2¼ parts by weight of crystals of sodium hyposulphite, 1 part by weight of crystals of copper sulphate. The salt present in the solution is probably $4Na_2S_2O_3, 3Cu_2S_2O_3 + xH_2O$.

After passing through the precipitation vats, it is converted by the sodium sulphide into ordinary sodium hyposulphite.

It was claimed for it that it dissolves metallic silver, silver sulphide, arsenical and antimonial minerals of silver, and other silver compounds more energetically than the sodium hyposulphite. "Based on this property of the 'extra solution,' it was claimed that silver ores treated by it required a less careful chloridizing-roasting, or only an oxidizing-roasting, and that even raw sulphide ores could be successfully desilverized." * These claims, however, have not been found in actual practice to be fully substantiated, the process has hence not been successful except in a few cases.

If the ore has been perfectly chloridized there is not much difference in the action of the two solutions.

The process is carried on in a similar manner to the Patera process, and with a similar but more extensive plant, with the exception that there is a special precipitation of lead. The operations are as follows :—

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* Hofmann, *op. cit.*, p. 251.

1. Chloridizing-roasting of the ore.

2. Transfer of the ore to the leaching vats (Fig 166), and washing with water to remove the salts of the base metals.

3 Precipitation of silver and copper from the wash-waters as in the Patera process.

4. As the "extra" solution is less energetic in its action on silver chloride than a solution of ordinary sodium hyposulphite, the ore is first leached with the latter solution, containing 0·7 to 1·8 per cent. of the salt. From the vats the solution is led to the lead precipitation vat, in which the lead chloride is precipitated as lead carbonate by sodium carbonate ; the precipitate also contains silver.

It is removed about once a week, pressed into cakes in a filter press, dried, and sold to smelters.

5 The clear solution from the lead-precipitating vat, after the precipitate has subsided, is run into the silver-precipitation vat.

6. The "extra" solution (containing about 2¼ per cent. hyposulphite and 1 per cent. copper sulphate) is run upon the ore, and the ordinary solution displaced. The discharge opening is then closed, and the extra solution either allowed to stand on the charge, or it is circulated by the Korting ejector.

7. The ore is now treated with successive water-washes, the solutions being led to the silver-precipitation vats.

8. The solutions are treated with sodium sulphide, and the precipitate, as well as that from operation 5, collected and converted into bullion, as described, p. 418.

The rate of leaching can be increased when necessary by means of the Korting ejector.

The Russell process, as compared with the Patera process, has the disadvantages of extra cost of chemicals required, greater complication in working, and extra plant ; and these are not always compensated for by the extra extraction of silver, which is sometimes but small.

(6) **Ziervogel Process.**—The process is specially adapted for the extraction of silver from argentiferous copper mattes containing about 50 to 60 per cent. of copper.

It has, however, been given up at most places, and is only in use at a few works, copper ores containing silver being now smelted for the production of metallic copper, from which the silver is extracted by electrolytic methods.

When argentiferous copper matte is cast in the usual sand moulds, in large pigs, there is a tendency during cooling for metallic silver to separate in fine filaments Hence all matte for the Ziervogel process should be cast in thin plates, so that it may cool rapidly, and this separation be prevented.

The operations of the process are as follows :—

1. Smelting the ore for the production of argentiferous matte.
2. Concentration of the matte to 60 or 70 per cent. Cu.
3. The first roasting of the ground matte.
4. Sulphating roasting of the finely ground product from the last operation.

5. Leaching the roasted matte with hot water, or hot water acidulated with sulphuric acid.
6. Precipitation of the silver by copper.
7. Washing and purifying the precipitated or cement silver.
8. Recovery of the copper from the liquors from the silver-precipitation vats.
9. Smelting the residues from the leaching vats for copper, or for matte to be treated for "bottoms" by the "best selecting" process for the extraction of the gold and some of the silver. The matte remaining to go to operation 4.
10. Electrolytic treatment of the "bottoms" from 9, for the separation of the gold and silver.
11. Refining the cement copper precipitated by iron.

A flow sheet of the process is given in Fig. 168.

The process is carried on as follows :—

The matte is crushed, passed through a 12-mesh sieve, and taken to the roasting furnace, which may be either a four-hearth reverberatory or other furnace. At Argo Pearce Turret furnaces were employed.

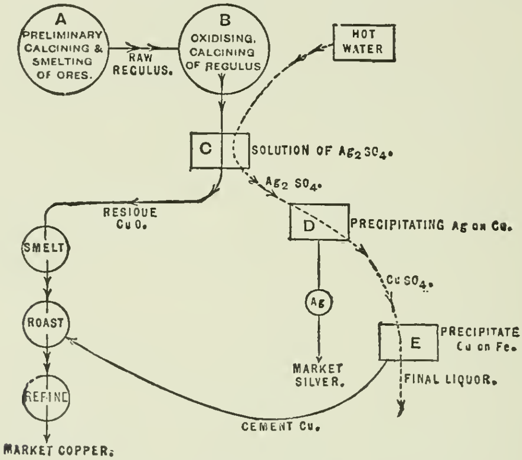
A
PRELIMINARY CALCINING & SMELTING OF ORES.
RAW REGULUS.
B
OXIDISING, CALCINING OF REGULUS
HOT WATER
C
SOLUTION OF Ag_2SO_4.
Ag_2SO_4.
RESIDUE CuO.
D
PRECIPITATING Ag on Cu.
$CuSO_4$.
SMELT
Ag
ROAST
E
PRECIPITATE Cu on Fe.
MARKET SILVER.
FINAL LIQUOR.
REFINE
CEMENT Cu.
MARKET COPPER.

Fig. 168.—Flow Sheet, Ziervogel Process.*

The object of the roasting is to oxidize the iron and copper sulphides of the matte, in order to obtain as much as possible of these metals, especially copper, as sulphates, and to leave about 5 or 6 per cent. of sulphur unoxidized. It is then roasted for the production of silver sulphate, in a small reverberatory furnace with a hearth about 11 feet 6 inches by 10 feet 6 inches, in charges of about 1,600 lbs.

First Stage.—The charge is kept at a low temperature for about $1\frac{1}{2}$ hours.

Second Stage.—The temperature is slightly raised and kept at a dull red heat with frequent stirring. During this stage it is endeavoured to form a maximum amount of iron sulphate and some copper sulphate, the silver remaining unchanged.

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* Roberts-Austen, *op. cit.*, p. 428.

Third Stage.—The heat is gradually increased for about an hour, and the iron sulphate is decomposed.

At about the end of the third hour the copper sulphate is at its maximum. It is decomposed during this stage, and silver sulphate is formed. By the end of the fourth hour the whole of the silver should have been converted into sulphate.

Fourth Stage.—During the last hour the charge is bruised with a heavy paddle to break up any lumps, and thoroughly worked about to oxidize any Cu_2O to CuO, and decompose almost but not all of the copper sulphate. During this stage tests are constantly made until the end of the operation. A sample of the hot charge is thrown into water in a small dish, when the water is raised to boiling and dissolves the silver sulphate and some copper sulphate. If, however, there is any Cu_2O present, it reduces the silver sulphate at once, metallic spangles being formed—

$$Ag_2SO_4 + Cu_2O = CuSO_4 + 2Ag + CuO.$$

As the operation proceeds the Cu_2O becomes gradually oxidized to CuO, and the spangles diminish.

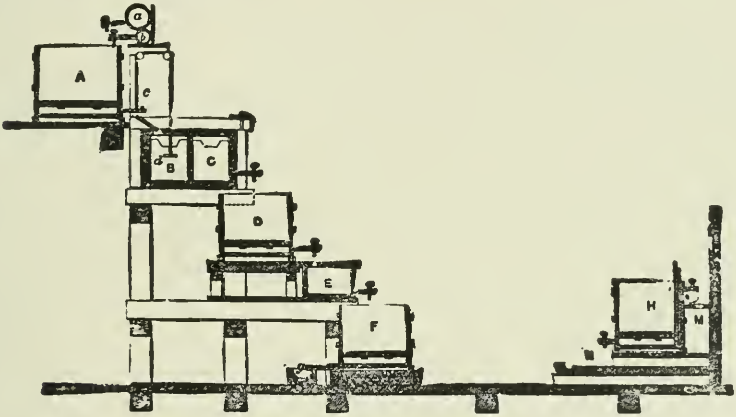

Fig. 169.—Ziervogel Plant.

During the last stage the whole of the Cu_2O has been oxidized, and the test shows no spangles, while the solution still remains of a pale blue colour, a small quantity of copper and other sulphates being always left to ensure that the silver sulphate is not itself undergoing decomposition. In spite of all care some silver remains in an insoluble form ; at Argo 45 ozs. per ton.

Leaching.—This is carried out in wooden tubs, provided with a double bottom, the upper being pierced with holes and covered with a cloth filter. They usually take a charge of 10 to 15 cwts. of the roasted matte (Fig. 169).

The charge is leached with hot water, sometimes acidulated with sulphuric acid. The tubs are kept constantly full, the solution being discharged through a cock into a series of tubs below. The time required for leaching is about eight or nine hours. The solution first enters a settling tub, and then passes to the silver-precipitating vats, which are sometimes long rectangular tanks about 4 feet wide, divided into compartments by diaphragms in such a manner that the solution passes alternately under and over them. Each compartment is nearly filled with copper plates, upon which the silver is precipitated. The solution from these vats runs into similar vats in front, which contain scrap iron for precipitating the copper, the liquors being run to waste.

The precipitated silver is transferred to a wooden tub with a false perforated bottom, and covered with dilute sulphuric acid. Steam and air are injected at high pressure below the false bottom, the silver is thus kept in violent agitation, and any copper or cuprous oxide it may be contaminated with are oxidized and dissolve in the sulphuric acid. At the end of the operation, the solution containing copper is run into the copper-precipitation vats. The silver is washed thoroughly with hot water, dried, melted in plumbago crucibles, and cast into ingots 999 fine.

The residue in the leaching tubs, which still contains silver, also any gold which may have been present in the ore, and is rich in copper, is smelted in a reverberatory furnace for the production of matte. If sufficiently rich in gold, the matte is concentrated and treated by the " best selecting " process (see p. 144) for its extraction, part of the silver being recovered at the same time.

About 5 to 5½ per cent. of the silver contents of a matte (144 ozs.) is lost by volatilization, from 3½ to 4 per cent. remains in the residue, and about 92 per cent. is recovered as cement silver (*Collins*).

(8) **Smelting Silver Ores with Lead Ores.**—When silver ores contain sufficient lead to enable them to be smelted for lead in the ordinary way, as described on pp. 192 to 221, the silver can always be most economically extracted by this method, wherever fuel is available or can be procured.

When silver ores do not contain sufficient lead to be smelted, and lead ores or lead-bearing material can be obtained sufficiently rich in lead to absorb and remove the whole of the silver on smelting, then smelting will usually be found to be an economical method of extracting the silver.

(9) **Matte Smelting of Silver Ores.**—By matte silver smelting is meant the smelting of silver ores, which are either free from lead, or do not contain it in sufficient quantity to collect the silver, but which contain pyrites, in order to produce a matte in which the silver may be concentrated. If the ore does not contain pyrites, pyritic ores must be obtained, and by preference such as are argentiferous or auriferous and contain copper. The matte smelting of silver ores is especially suitable in localities where lead ores or lead-bearing materials cannot be obtained, and where cupriferous pyrites is available.

By the introduction of pyritic smelting and the electrolytic processes of separating the precious metals from copper, this method of extracting silver from ores has been greatly stimulated, and has been made possible in districts where formerly it could not be economically carried out.

Argentiferous pyritic ores containing from 3 to 4 per cent. of copper or less are especially valuable, even when they contain only a little silver and a little gold, as they admit of the concentration of these metals in a small quantity of matte, and will hence pay to work.

The ore should not contain much zinc blende, and the slag should be highly siliceous. Under these conditions there will not be much loss of either gold or silver.

So that, speaking generally, an ore, or a mixture of ores, of the above composition, containing only a few ounces of silver and a few grains of gold, will pay to smelt, as with proper charges and slags the metals in 10 or 12 tons of ore may be concentrated in 1 ton of matte.

The ores or mixture of ores need not contain as much copper as 3 per cent.; they must, however, contain some, as a simple iron matte will not contain the whole of the precious metals present, but more or less will pass into the slag.

According to Austin * and other metallurgists, 0·5 per cent. of copper in the ore is sufficient to collect the silver and gold, whilst Peters † considers about two-thirds of 1 per cent. as "the amount of copper in the furnace charges which is sufficient to make a satisfactory collection of the gold and silver under favourable conditions." The smelting is carried out as described under Copper, pp. 94 and 112, preferably by the pyritic method, and the matte obtained converted by Bessemerizing into copper, from which the silver and gold are separated as described on pp. 169 to 174.

Toughening and Refining Silver.—The impurities which the author has found present in silver bullion of high fineness, over 990 per 1,000, are Pb, Cu, Bi, and Hg. In some consignments to the Imperial Japanese Mint from Korea, Zn was also present. The bullion was sometimes brittle, generally from the presence of Bi, either before or after melting with copper to form the coinage alloy 900 fine. This brittleness was easily removed by exposing the metal whilst molten to a current of air with occasional additions of nitre and of bone ash, the latter being added first. The addition of bone ash not only facilitated the skimming off of the slag which was formed, but it also protected the crucible from being corroded.

For the refining and parting of silver, see under "Gold," pp. 357 to 372.

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* T. A. Rickard, *Pyrite Smelting*, p. 18.

† Peters, *Principles of Copper Smelting*, p. 415.

PLATINUM.

Physical Properties.—Platinum is a white metal with a greyish tinge, and takes a high polish, but is less brilliant than silver. It is very malleable and ductile, and can be rolled into thin sheets and drawn into fine wire. These properties are impaired by the presence of impurities, and small quantities of other metals of the platinum group reduce the ductility.

Platinum is harder than copper, silver, or gold, and possesses a tenacity when in the form of wire of about 11½ tons per square inch.

The specific gravity of cast platinum is 21·5 (*Deville* and *Debray*).

Its electric conductivity is low, being only 13·4 at 0° C. when silver = 100.

Its coefficient of expansion is also low, and is less than that of any other metal. As it is about the same as that of some kinds of glass, platinum wires can be fused into glass tubes or vessels without causing them to crack on cooling or under variations of temperature.

Platinum melts at about 1,755° C. The melting point is lowered by the presence of most other metals.

In the electric furnace platinum volatilizes readily (*Moissan*), and Sir William Crookes has shown that the metal is sensibly volatile at 1,300° C.*

At a temperature approaching whiteness it can be welded.

When molten it absorbs oxygen, and if rapidly cooled gives off the gas with such violence that it " spits " like silver.

Oxygen and hydrogen are both occluded by platinum foil, the latter to a much greater extent than the former, as much as 200 volumes being absorbed under special conditions.

When platinum is precipitated from dilute solutions by reducing agents or metals it is obtained in the form of a very finely divided black powder, which is known as *platinum black.* Platinum in this form is capable of absorbing very much larger quantities of gases, and when charged with oxygen acts as a powerful oxidizer.

The atomic weight of platinum is 195·2.

Chemical Properties.—Platinum is not acted on by dry or moist air, even when heated to high temperatures. It is not attacked by hydrochloric, nitric, or sulphuric acid, but when alloyed with silver, copper, lead, zinc, and some other metals it is partly dissolved by nitric acid. At high temperatures it is oxidized by fused alkalies in the presence of air, and by potassium and other nitrates when air is excluded. It is also attacked at high temperatures by carbon, and by silica in the presence of carbon. Platinum vessels should, therefore, never be heated in contact with solid fuel. Cyanides likewise attack it.

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* *Proc. Royal Soc.*, 1912, vol. lxxxvi, p. 464, *et seq.*

As platinum more or less readily forms alloys with many metals, neither they nor easily reducible oxides should be melted in contact with it, as in platinum crucibles, basins, etc.

When treated with *aqua regia* or other mixtures which evolve chlorine, platinum dissolves with the formation of $PtCl_4$. It is, however, less soluble in *aqua regia* than gold, and the author has dissolved crusts of gold which had adhered to the platinum boilers used in gold refining by dilute *aqua regia* without dissolving much platinum.

When the *aqua regia* solution of platinum is evaporated to expel nitric acid, with frequent addition of hydrochloric acid, H_2PtCl_6, to which the name *platini-chlorhydric acid* is applied, is obtained as crystals.

Platinum tetrachloride, $PtCl_4$, is formed by heating H_2PtCl_6 to 165° C. in a stream of dry HCl.

Platini-chlorhydric acid, H_2PtCl_6, is formed as described above. The crystals are red-brown, deliquescent, soluble in water and alcohol, and are decomposed by heating to about 230° C. Platinum is precipitated from its solution in the metallic state by magnesium, iron, formates, and similar reducing agents, and by ferrous sulphate after long boiling.

It is of great importance in the metallurgy of platinum, as it forms double salts with potassium and ammonium chlorides, which are only slightly soluble in water, and are insoluble in alcohol. Platinum is thus separated from solutions containing it and other metals. When ammonium chloride or potassium chloride is added to cold solutions of platinum chloride, yellow crystalline precipitates of ammonium platini-chloride, $(NH_4)_2PtCl_6$, and potassium platini-chloride are respectively produced. Both are practically insoluble in alcohol, and but very slightly soluble in water, the ammonium salt being least soluble. When the ammonium salt is heated to redness it is reduced and pure spongy platinum is left as a residue, whilst in the case of the potassium salt the residue consists of spongy platinum mixed with potassium chloride.

Platinum and its Alloys.—Platinum as met with in the forms of foil, wire, crucibles, and other vessels is free from injurious impurities.

Owing to its resistance to the action of acids and most chemical agents, even at high temperatures, and to its high melting point, it is in extensive use for the manufacture of crucibles, basins, foil, wire, etc., and for chemical laboratory work.

A large quantity of platinum is also used in the construction of apparatus for the concentration of sulphuric acid, and as spongy platinum in the manufacture of sulphuric acid and of nitric acid from ammonia by catalytic methods.

A considerable amount is consumed in the electrical and dental industries, and in the preparation of salts, notably the chloride for photographic work. At the present time there is also a large demand from jewellers, the fashion being to substitute platinum for gold in certain kinds of work.

Coins of platinum were struck by the Russian Government between

1828 and 1841, but owing to the cost and difficulties attending the melting of the metal and the rapid fluctuations in its value its coinage was discontinued.

Platinum forms alloys with a number of metals, but only a few are of industrial importance. The most important alloys are those with gold, iridium, palladium, osmium, rhodium, ruthenium, silver and nickel.

Platinum and Iridium.—These alloys are very hard and elastic, unalterable in the air, and take a high polish. An alloy of platinum 90, iridium 10, was prepared by Johnson and Matthey in 1870 for the Comité International des Poids et Mesures for the standard metre. Subsequently George Matthey recommended the alloy containing 15 per cent. of iridium for standard measures of length, made in the tubular form, and the 20 per cent. alloy for standard weights.

Platinum with 10 per cent. of iridium is largely used as one of the wires in thermo-couples intended for the measurement of high temperatures, the other wire being of pure platinum. An alloy of platinum with 10 per cent. of rhodium is used for the same purpose.

Platinum and copper unite in all proportions, giving yellow or white alloys, according to the percentage of copper present. "Cooper's gold," containing 81·25 per cent. of platinum and 18·75 per cent. of copper, is a golden yellow alloy taking a high polish and closely resembles 18-carat gold.

Platinum and Silver.—Platinum alloys with silver in all proportions.

An alloy of 34 per cent. of *platinum* and 66 per cent. of *silver* is employed as a standard of electrical resistance.

An alloy used by dentists contains from 20 to 30 per cent. of platinum.

Hot concentrated sulphuric acid dissolves the silver in platinum-silver alloys, leaving the platinum undissolved. When they are acted on by nitric acid the silver is dissolved and also part of the platinum. If they contain less than 10 per cent. of platinum both the silver and the platinum are dissolved.

Platinum and lead form alloys which melt at comparatively low temperatures, and from which the platinum can be separated by cupellation. The last portions of lead, however, cannot be removed at the temperature of an ordinary muffle, and an oxyhydrogen flame is necessary to complete the operation.

Platinum and Iron.—According to Faraday and Stodart, platinum and steel alloy well together in all proportions.* Several of the alloys are malleable. With 10 per cent. of platinum rusting is prevented. An alloy with smaller percentages was used in the manufacture of non-rusting cutlery.

Platinum and mercury do not unite to form amalgams in the ordinary way, but amalgamation may be promoted by the use of certain activating agents, *e.g.* zinc amalgam, copper sulphate and sulphuric acid.

Platinum and gold, see p. 254.

Platinum Substitutes.—Research has not yet produced a substance which in all its properties can serve as a general substitute.

Alloys of gold and palladium are found to offer the greatest possibilities. The chemical properties of this series of alloys, to which the name "rhotanium" has been applied, are, with the exception of resistance to strong nitric acid, equal to those of platinum.

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* Percy, *Iron and Steel*, p. 178.

An alloy containing about 11 per cent. Pt and 89 per cent. Au is being made under the trade name " Platino." The alloy is said to be more resistant to caustic potash than platinum ; it is, however, attacked by sulphuric acid containing nitric acid. It is said to resist attack by fused potassium nitrate.

Ores of Platinum.—Platinum occurs native as metal in the form of grains approximately spherical, less often flattened, in alluvial deposits derived from the disintegration of primitive rocks. It is also found in the primary dunite occurrences in the Urals and in many of the ultra-basic and basic igneous rocks of South Africa.

Nuggets are rare, but one of unusually large size, weighing 270 ozs., is recorded by Hautpick * as having been found in the placers of Mt. Katchkonara, in the Northern portion of the platiniferous district of the Urals, Russia. A still larger one, weighing 21·64 lbs., is in the Demidoff Museum, Petrograd.

The best known deposits of platinum are the alluvial sands of the Urals. They are contained within a length of about 80 miles along the Central part of the chain in the Government of Perm, the principal centres of the placers being at Blagodat on the Eastern and Nijni Tagilsk on the Western slopes, and formerly furnished the main part of the world's production of the metal.

Platinum is associated in the placers chiefly with gold, iridosmine, chromite, magnetite, zircon, ilmenite, corundum, and quartz. The admixture of gold is very variable, ranging from 2 or 3 per cent. in some districts to as much as 20 or 25 per cent. in others.

The platinum, together with the gold and iridosmine, when the last is present, is separated from the sand and associated minerals by a series of washing processes ; subsequently the product is treated with mercury for the separation of the gold.

The crude platinum thus obtained contains from about 71 to 89 per cent. of the metal. It is invariably alloyed with iron in considerable proportions, and with varying amounts of the metals of the platinum group.

Analyses of Crude Platinum from Various Parts of the World.†

	California.	California.	British Columbia.	Colombia.	New South Wales.	Tasmania.	Russia.	Oregon.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Pt. .	85·50	63·30	72·07	80·00-86·20	75·90	61·40	76·16-83·50	61·45
Ir, .	1·05	0·70	1·14	0·85- 1·55	1·30	1·10	1·38- 2·74	0·40
Rh, .	1·00	1·80	2·57	1·40- 2·50	1·30	1·85	0·30- 0·69	0·65
Pd, .	0·60	0·10	0·19	0·35- 1·00	trace	1·80	0·18- 0·30	0·15
Iridosmine.	1·10	22·55	10·51	0·95- 1·40	9·30	26·00	0·79- 4·99	27·30
Au, .	0·80	0·30	..	1·00- 1·50	..	1·20	0·07- 0·27	0·85
Fe, .	6·75	6·40	8·59	7·20- 8·03	10·15	4·55	7·68-14·72	4·30
Cu, .	1·40	4·25	3·39	0·40- 0·65	0·41	1·10	0·54- 3·39	2·15
Sand,	2·95	..	1·69	0·40- 4·35	1·22	1·20	..	3·00
	101·15	99·40	100·15		99·58	100·20		100·25

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* *Min. Journ.*, April, 1910, p. 483.

† J. M. Hill, *Eng. and Min. Journ.*, July, 1919.

Platinum metals are also found in less important quantities in Colombia, South Africa, California, Oregon, Alaska, Brazil, New South Wales, Borneo, and New Zealand. Of these countries, Colombia and South Africa are the most important producers. The platiniferous gravels cover a considerable area in the Chocos and Barbacoas districts in the Western part of Colombia, but practically the entire product comes from the former. The crude platinum occurs in these gravels associated with gold, and with the same minerals, and in the same forms as in the Urals, and has a similar composition.

In recent years South Africa has become an important producer of the platinum metals.*

Platinum also occurs in combination with arsenic as the mineral sperrylite ($PtAs$) in the nickeliferous pyrites of Sudbury (Canada), and in the treatment of these ores a considerable quantity of the metal is obtained.

As regards the relative amounts of platinum produced in the various centres of production, Russia decidedly came first in 1914, with about 95 per cent. of the total production of the world, the output, chiefly from the placers in the Urals, being about 241,000 ozs.

The quantities of platinum metals produced in 1927 in the following countries have been estimated in the Statistical Summary of the Imperial Institute as under :—†

Canada,	22,773 ozs.
Colombia,	55,000 ,,
Russia,	100,000 ,,
United States,	46,459 ,,
South Africa,	25,043 ,,

The figure for the United States includes 46,050 ozs. recovered by refineries.

The Extraction of Platinum.—The crude platinum is separated from the sands and gravels, as already stated, by a series of washing processes. If any gold is present it is obtained in the concentrate together with the platinum.

In Russia the gold is removed by repeated amalgamation with mercury in wood, iron, or porcelain bowls, about 10 to 30 lbs. being treated at a time. The crude platinum is then refined.

In the treatment of the ores of the dunite deposits of the Lydenburg ‡ district of S. Africa at the Onverwacht plant, the ore is crushed in a Blake crusher and then in Californian stamps. The pulp passes to the cone of a 5 feet by 4 feet 6 inches tube mill through a trap for catching metallics; the underflow passes through the mill to Wilfley tables and the overflow to slime tables and thence over corduroy tables. The metallics from the tables are hand-panned and then treated successively with 10 per cent. sulphuric acid and 10 per cent. nitric acid, washed, dried, weighed, and despatched to the refinery as coarse crude platinum, assaying about 82 per cent. of platinum metals. The concentrates from the Wilfley tables, slime tables and corduroy tables are treated in lots of 1,000 lbs. in an amalgamating barrel, the amalgamation of the platinum being promoted by activating agents such as zinc amalgam, copper sulphate or sulphuric acid. The barrel is revolved for two hours and the dirty amalgam obtained is re-amalgamated, pressed, and treated with sulphuric acid for removal of zinc and iron. It is then retorted and the retort sponge treated with acid, washed, dried, and shipped to refiners.

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* P. A. Wagner, *Platinum Deposits and Mines of South Africa*, Oliver & Boyd, 1929.

† *The Mineral Industry of the British Empire and Foreign Countries* (*Statistical Summary*, 1928), p. 267.

‡ T. K. Prentice and R. Murdoch, *Journ. Chem. Met. Min. Soc., S. Africa*, 1929, vol. xxix., pp. 157-166. See also paper by J. E. Healey and T. K. Prentice on "Mining and Recovery of Platinum at Onverwacht Platinum Ltd.," read before the *Third Empire Mining and Metallurgical Congress, S. Africa*, 1930.

At the Maandagshoek plant * the ore is crushed in a Hadfield jaw-crusher, disc crusher and ball mill, the resultant pulp being concentrated on Fraser and Chalmers' tables. The tails are classified, the underflow being re-ground in a ball mill; the resulting pulp is thickened, made to flow over corduroy tables and passed to a sub-aeration flotation unit.

The table heads and corduroy concentrates are treated on James' sand and slime tables respectively for extraction of metallics, which are acid-cleaned, washed and dried; they assay about 60 per cent. platinum metals and are sent to the refinery.

The treatment of the sulphide ores of the Merensky Horizon consists in the flotation of the nickel-copper sulphide minerals which carry the platinum metals, and smelting the product to a low grade nickel-copper-iron matte. This matte is re-smelted to produce a higher grade matte containing about 25 per cent. nickel, 15 per cent. copper and 70 ozs. of platinum metals per ton. This second matte is roasted and the oxidized material leached with sulphuric acid for solution of the oxides of the base metals; the residues are worked up for platinum. There are a number of processes, some patented, which have been suggested for the treatment of the matte.

A chlorination process has also been developed for the sulphide froth-flotation concentrate obtained from Norite ores. This process has been described by R. A. Cooper and F. W. Watson,† who state that the froth-flotation effects an 87 per cent. extraction of the platinum metals in a concentrate weighing about 5 per cent. of the ore and assaying 7·5 to 10 ozs. per ton. After roasting to remove sulphur, the concentrates are mixed with 15-20 per cent. of sodium chloride and heated to 500°-600° C. in an atmosphere of chlorine for four hours. The product is only slightly caked and is readily leached to give a solution containing over 90 per cent. of the platinum metals and over 80 per cent. of the copper and nickel present. The gold in the residue, together with some of the remaining platinum and palladium, may be recovered by cyanide leaching. The chloride solution is agitated with powdered limestone (20 lbs. per ton of solution) to precipitate copper carbonate containing about 2 ozs. of platinum per ton, which may be recovered by smelting the precipitate to copper and electrolysing. The filtrate is agitated with zinc dust and a little hydrochloric acid to precipitate the platinum metals and the filtrate from these treated with bleaching powder to recover the nickel.

The Ehlund amalgamation process may be applied directly to oxide or sulphide ores, or to concentrates. It consists in bringing the finely divided mineral into contact with zinc amalgam in the presence of an activator, the platinum metals being thus amalgamated and retained by the amalgam. The activator used consists of an aqueous solution of mercuric chloride, zinc

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* *Mining and Industrial Magazine of South Africa*, Aug., 1928, p. 585. See also paper by F. Wartenweiler and A. King on "The Metallurgy of Transvaal Platinum Ores," read before the *Third Empire Mining and Metallurgical Congress, S. Africa*, 1930.

† *J. Chem. Met. Min. Soc., S. Africa*, 1929, vol. xxix., pp. 220-228.

chloride, hydrochloric acid or chlorine, with or without the addition of sodium chloride. The ore is ground to about 200 mesh in a solution which has previously passed through the process and contains these activators, a small amount of hydrochloric acid added to the pulp, which is passed over an iron or nickel surface coated with zinc amalgam, which retains the platinum metals. The amalgam is removed from time to time and retorted in the usual way.

Refining.—The crude platinum can be refined either by dry or by wet methods. When dry methods are employed the platinum will contain iridium and rhodium; on the other hand, when wet methods are used, the resulting platinum will be pure. A combination of the two methods is also employed.

The wet methods consist essentially in dissolving the crude platinum in *aqua regia*, precipitating the platinum as ammonium platini-chloride, heating the precipitate to redness, forming spongy platinum, and fusing the latter by the oxyhydrogen blowpipe in a furnace constructed of blocks of lime. The operations are as follows :—The crude platinum is digested in *aqua regia* containing an excess of hydrochloric acid in porcelain vessels heated by means of a sand-bath.

A solution is thus obtained of platinum and small quantities of the metals of the platinum group, osmiridium and sand, etc. remaining undissolved. The solution is repeatedly evaporated with additions of hydrochloric acid to expel nitric acid. It is then diluted with water and filtered from the undissolved residue. To the cold clear solution a solution of ammonium chloride is added and ammonium platini-chloride precipitated as a yellow crystalline precipitate. A small quantity of the corresponding iridium salt also comes down.

The precipitate is washed and dried, and then gradually heated to redness in a muffle, when ammonium chloride and chlorine are driven off and spongy platinum remains—

$$(NH_4)_2PtCl_6 = Pt + 2NH_4Cl + 2Cl_2.$$

The spongy platinum is broken up by rubbing, sifted, made into a paste with water, and strongly compressed in a steel mould by means of a piston and repeated blows with a heavy hammer. The mass thus obtained can be heated to a welding temperature, and by repeated hammering and heating be forged into a bar, or it may be melted by the oxyhydrogen blowpipe in a small furnace made of blocks of lime.

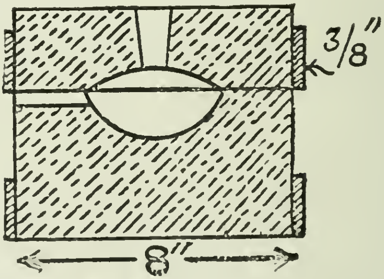

Fig. 170.—Melting Furnace for Platinum.

The furnace (Fig. 170) is constructed of two blocks of lime bound with hoop iron. In the upper block there is an opening for the admission of the blowpipe flame. The lower block contains the cavity in which the platinum is melted, and on one side of its upper edge there is a groove through which the molten metal is poured.

The furnace rests on an iron plate, so arranged that it can be tilted when the platinum has to be poured. Oxy-coal gas is usually employed instead of oxyhydrogen.

The metal thus obtained always contains some iridium, about 2 per cent., which has been precipitated with the platinum, and a second refining is required for its removal.

The filtrate from the ammonium platini-chloride precipitate, which still contains platinum, iridium, and the associated metals, is treated with metallic iron and the precipitated metals after digestion with hydrochloric acid, to remove iron, are dissolved in *aqua regia.* Ammonium chloride is added to the solution, and more platinum and iridium are recovered. The filtrate from this precipitate contains nearly the whole of the Rh, Ru, Pd, and a little of the As which may have been present in the crude platinum, and is treated for the recovery of these metals by chemical methods.

The foregoing operations represent generally the procedure followed in the wet way for the extraction of platinum from the crude metal, but, as pointed out, it is evident the result is not a perfectly pure metal, but platinum which may contain small amounts of iridium, rhodium, and palladium, yet is sufficiently pure for most purposes.

MERCURY.

Physical Properties.—Mercury, or, as it is called, quicksilver, is the only metal which is liquid at common temperatures.

When it is agitated with oils or grease, or in the presence of compounds of arsenic and antimony, it is converted into a fine powder consisting of minute globules of the metal not easily reunited. This is known as "flouring," and is one of the causes of the loss of mercury in stamp-milling.

Action of Heat.—The boiling point of mercury is 360° C., but it is slightly volatile at ordinary temperatures. It solidifies at $-39°$ C., forming a tin-white ductile and malleable metal. Its conductivity for heat is lower than that of any other metal.

Specific Gravity.—Its specific gravity is 13·59.

Electrical Conductivity.—Its electrical conductivity is very low, being only 1·6 if that of silver be taken as 100.

Atomic Weight 200·6.

Chemical Properties.—Pure mercury is unaltered on exposure to air at ordinary temperatures, even in the presence of moisture, but when it is impure from the presence of other metals it is oxidized, and its surface becomes covered with a grey powder.

Mercury is insoluble in dilute hydrochloric and sulphuric acids. It is, however, soluble in nitric acid, even when dilute, and in hot concentrated sulphuric acid. *Aqua regia* converts it into the chloride, $HgCl_2$.

The oxides of mercury are of no metallurgical importance.

Mercury Chlorides.—There are two chlorides—namely, mercurous chloride, Hg_2Cl_2, and mercuric chloride, $HgCl_2$. The former is insoluble and the latter soluble in water. Mercurous chloride (calomel) is often formed in the amalgamation of gold and silver ores when chlorides are present, and is one of the causes of the loss of mercury in the operation.

Mercuric Sulphide, HgS.—Mercuric sulphide is the most important compound in the metallurgy of mercury. It occurs native as cinnabar, which is the chief source of the metal. Mercuric sulphide volatilizes unchanged if air be excluded, but when heated with access of air the sulphur is oxidized to SO_2, and metallic mercury distils over.

It is also decomposed when heated with lime and with metals which have a greater affinity than mercury for sulphur.

It is insoluble in hydrochloric, nitric, and sulphuric acids, but soluble in *aqua regia,* and in solutions of potassium and sodium sulphides.

Mercury and its Alloys (amalgams).—Mercury is placed on the market in wrought-iron flasks closed with a screw plug and containing 75 lbs. of the metal.

As ordinarily met with in commerce it is usually nearly pure, but sometimes it contains traces of foreign metals, those of most frequent occurrence being lead and zinc.

A rough test of its purity is to allow a small particle to run down a slightly inclined glass plate, when if impure from the presence of lead or other metals, the globules will assume a pear-like shape or leave a "tail." Only pure mercury will form spherical globules which unite at once on being brought into contact with one another. It should leave no film on rough filter paper.

In the amalgamation of gold and silver ores the mercury employed gradually becomes contaminated with foreign metals, and requires to be purified from time to time.

The treatment to which it should then be subjected for purification is described under "Gold Milling," p. 264.

Mercury is employed in the amalgamation of gold and silver ores; the quantity used for this purpose is, however, rapidly decreasing, owing to the advance of the cyanide process. The construction of scientific instruments, barometers, thermometers, rectifiers, mercury-vapour lamps and storage batteries, the "silvering" of mirrors, and the preparation of vermilion and medicinal compounds also consume a not inconsiderable amount of the metal. There is also a demand for the manufacture of fulminate of mercury for fuses in blasting. Mercury combines readily with many metals, such as potassium, sodium, gold, silver, tin, zinc, lead, and bismuth, forming alloys which are known as amalgams; it will not, however, unite directly with platinum, iron, aluminium, chromium, manganese, nickel, and cobalt. All amalgams are white, and are solid, pasty, or liquid, according to the less or greater proportion of mercury they contain. They mix with mercury in all proportions, and are more or less soluble in it.

When mercury containing an amalgam is squeezed through canvas, an amalgam of approximately definite composition is left behind, and the mercury passing through retains as much of the amalgam as it is capable of holding in solution at the temperature at which the filtration was carried out. When the amalgams of gold, silver, and the heavy metals are heated to the boiling point of mercury, the mercury distils off, leaving the other metals behind. From all amalgams mercury can be separated by distillation. It is on these properties that the extraction of gold and silver from their ores by amalgamation depends.

Ores of Mercury *—*Native Mercury.*—Mercury occurs in the state of metal generally in small globules in several localities associated with cinnabar, but never in important quantities.

Cinnabar, Mercury Sulphide, HgS.—It contains when pure 86·2 per cent. of mercury. Its red colour and high specific gravity, about 8·0, are specially characteristic. In rare cases, however, it is almost black, and may be overlooked in ores when present in small amounts. Thus, in Hungary a fahl ore containing mercury was worked only for copper and silver for many years before the presence of mercury was detected. Therefore, in the examination of ores, heating in a bulb tube and in one open at both ends, should never be omitted.

Cinnabar is the only important ore of mercury. It occurs chiefly associated with sandstones, limestones, cretaceous and bituminous shales, etc., in veins or lodes, and often disseminated in minute grains through sandstones. In Texas it is found in bituminous shales. Fahl ore and blende sometimes contain mercury. The localities where it is mined in the largest quantities are, in Europe, Almaden (Spain), Idria,† and Monte Amiata (Italy); in the

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* *Mercury Ores*, by E. Halse, Imp. Inst. Monograph on Mineral Resources, 1923.

† Austrian until Nov. 12, 1920.

United States, California, and Texas; and at Guerrero in Mexico, Kweichow in China, and in the district of Ekaterinoslaf in Russia.

The other minerals of mercury are of no metallurgical importance.

It is generally agreed that cinnabar and other minerals containing mercury have been deposited from aqueous solution and evidence in support of this is afforded by the nature of the associated gangue minerals and by the fact that mercury minerals are found in the vicinity of hot springs or in regions which show signs of the former existence of such springs. Cinnabar and minerals usually associated with it are soluble in alkaline sulphide solutions, which are frequently present in deep-seated underground waters. From these solutions the cinnabar can be precipitated by dilution or by the action of bituminous shales, etc.

Mercury ores are seldom found massive, but generally in the form of narrow veins or as disseminations or impregnations in siliceous or limestone rocks; this necessitates the mining of a large amount of useless material, and the average mercury content of the ore sent to the reducing furnaces is seldom more than 1 per cent. Mercury minerals, although of high specific gravity, give trouble in wet methods of concentration, as they form a considerable proportion of slime when crushed, and this slime is difficult to recover by wet methods; nevertheless these methods are sometimes used.

The Extraction of Mercury.—From what has already been stated, it is obvious that cinnabar is practically the only ore from which mercury is extracted, but it often contains the native metal.

In this connection it must be remembered that extremely poor ore can be profitably worked; thus, if cinnabar is distinctly visible in any rock mass, it will almost certainly pay to work it. The main bulk of the mercury produced in the world is obtained from ores containing from 0·5 to 1·0 per cent. of the metal. The average yield in the United States in 1910 was 0·6 per cent. In California at present an ore assaying 0·75 per cent. is considered comparatively rich.

The extraction of mercury is always carried out in the dry way. For a wet method, see p. 547.

As cinnabar (HgS) is only partially decomposed when heated with carbon, some reagent must be employed which will oxidize the sulphur to SO_2, or combine with it to form a sulphide. The process, for the extraction of mercury from it, are, therefore, based on the reactions expressed by the following equations :—

$$\begin{aligned}&(1)\quad HgS + 2O &&= Hg + SO_2.\\&(2)\quad 4HgS + 4CaO &&= 4Hg + 3CaS + CaSO_4.\\&(3)\quad HgS + Fe &&= Hg + FeS.\end{aligned}$$

It follows that the operations necessary consist in reduction of the sulphide, and, as they take place at a temperature higher than the boiling point of mercury, in the volatilization of the metal and its condensation.

As a general rule, the process based on the reaction in the first equation is the most convenient and best, and except for the occasional treatment of rich ores and materials, it is that which is everywhere employed. It may be termed the "*air-reduction*" process.

The process has, however, one disadvantage, the vapour of the mercury is diluted with SO_2, the gaseous products of combustion and excess of air, it is hence difficult to condense; and always more or less of the condensed mercury is obtained in the form of mercurial soot, a mixture of finely divided metal and sooty matter from the fuel which requires special treatment. According to Spirek, however, the soot, although it complicates the work, aids in the condensation and collection of the extremely fine particles of mercury which would otherwise be lost.

The preparation of the ores for furnace treatment is of special importance in the metallurgy of mercury. It may be laid down, as a rule, that they should not be prepared by wet concentration, on account of the cost, and especially the losses liable to occur, also the difficulty of dealing with the tailings from the dressing operations, which will generally contain 0·6 to 1·0 per cent. of mercury, or even more.

Experiments by Walter W. Bradley,* of the staff of the Mining Bureau at the University of California, however, have shown that high extraction (above 90 per cent.) can be obtained, by water concentration on tables, with friable ores, in which the cinnabar is distinctly crystalline. Crushing by rolls produces a minimum of slime. If, however, the pulp contains a cinnabar slime, or if it is necessary to crush fine to release the sulphide, the extraction by tables will be low. In such cases it can be improved by classification, and treating the different sizes on separate tables. The slimed cinnabar can be recovered by flotation. A high extraction has been obtained by flotation tests in finely ground (80-mesh) fresh ores, utilizing either pine-oil derivatives or eucalyptus oils. "Fresh" ores are specified, because, contrary to common conception, cinnabar on exposure does oxidize sufficiently to affect flotation results, as some of these tests have indicated. Good results were obtained by table concentration on an ore carrying natural quicksilver.

Water concentration is now in operation at the Oceanic, New Almaden, New Idria, and other mines in California. Many experiments have been made in the use of flotation, and plant installed at New Almaden proved that flotation alone did not give as good a result as tables alone.

In the best modern practice the rich portions of the ore are separated usually at the mine by spalling and hand picking. The poorer ore remaining is then classified by screens or trommels into "coarse" and "fine," the former consisting of pieces of about 1½ inches and upwards in size, and the latter of pieces of less than 1½ inches. The fine ore is again divided in some works into "medium coarse" and "fine." Speaking generally, these various classes are treated as follows :—

The coarse ores in shaft furnaces, both in Europe and America.

The medium coarse ore in shaft furnaces in America, but in Czermak-Spirek shelf- or tile-furnaces in Europe.

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* *Min. and Sc. Press*, May, 1916.

The fine ore in reverberatory furnaces in Europe, if not too poor.

When the fine ore is not separated into medium, coarse, and fine, it is treated in shaft furnaces in America, and in Czermak-Spirek tile furnaces in Europe.

Revolving cylindrical furnaces and the MacDougall type of furnace have been used in America.

The rich ore is either treated in retorts, as in America, or in small Czermak-Spirek tile furnaces in Europe.

The "Quicksilver Resources of California," by Walter W. Bradley, Bulletin No. 78 of the California State Mining Bureau, published in 1918, contains valuable information on the metal, and should be consulted by all who have to deal with its metallurgy. The following remarks are a brief abstract of the section relating to the extraction and condensation of the metal.*

"An experimental revolving cylindrical furnace was erected by Mr. H. W. Gould in 1918 at the New Idria Mine, San Benito County, and it is thought that this type of furnace has great possibilities for the treatment of mercury ores. Thus far, it appears that the cost of such furnaces is one-fourth to one-half that of the Scott per ton-day-capacity; consumption of fuel one-third to one-half; labour one-fifth to one-half. It is more flexible than the Scott; the ore passes through in 15 to 30 minutes, with all of the mercury apparently expelled. There are no absorption losses in the furance, as all the bricks are hot. There is no personal element attached to the rotary, the feed and discharge being automatic, as against the irregularities possible with the hand labour on a Scott.

"Salivation of the workmen cannot result from the end ports of the furnace, because of the inward suction due to the stack draught."

As regards working costs, the Scott furnace seems to have an advantage, as no skilled labour and no power are required, and it may be worked either with wood or oil, while the rotary has not been successful except with oil fuel. On the other hand, the rotary furnace has an advantage in that wet or damp ores can be treated directly, whereas the Scott does not work satisfactorily except when a drier is used.

"This first furnace was 4 feet diameter and 50 feet long, arranged to drive at 1½ to 4 revolutions per minute. It was handling 72 tons of ore per day of 1½-inch size; a more economical size for the ore is probably ¾-inch to 1 inch.

In Fig. 171 is shown the arrangement of the rotary furnace and the condensers. Several of these furnaces have been built 56 feet long and 5 feet in diameter. They have not proved satisfactory with all classes of ore.

In the condensing system the mercurial fume passes through the following in succession:—A dust chamber, vitrified-pipe flue, brick condenser, cast-iron condenser, vitrified-pipe flues, and finally tank-type condensers of wood. The fan shown above the dust chamber is for blowing cold, moist air into the condensing system. "One of the most interesting recent developments concerned with condensation at the New Idria mine is this introduction of a stream of cold, moist air into the flue leading from the first brick condenser."

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* *Opus cit.*, pp. 247-252.

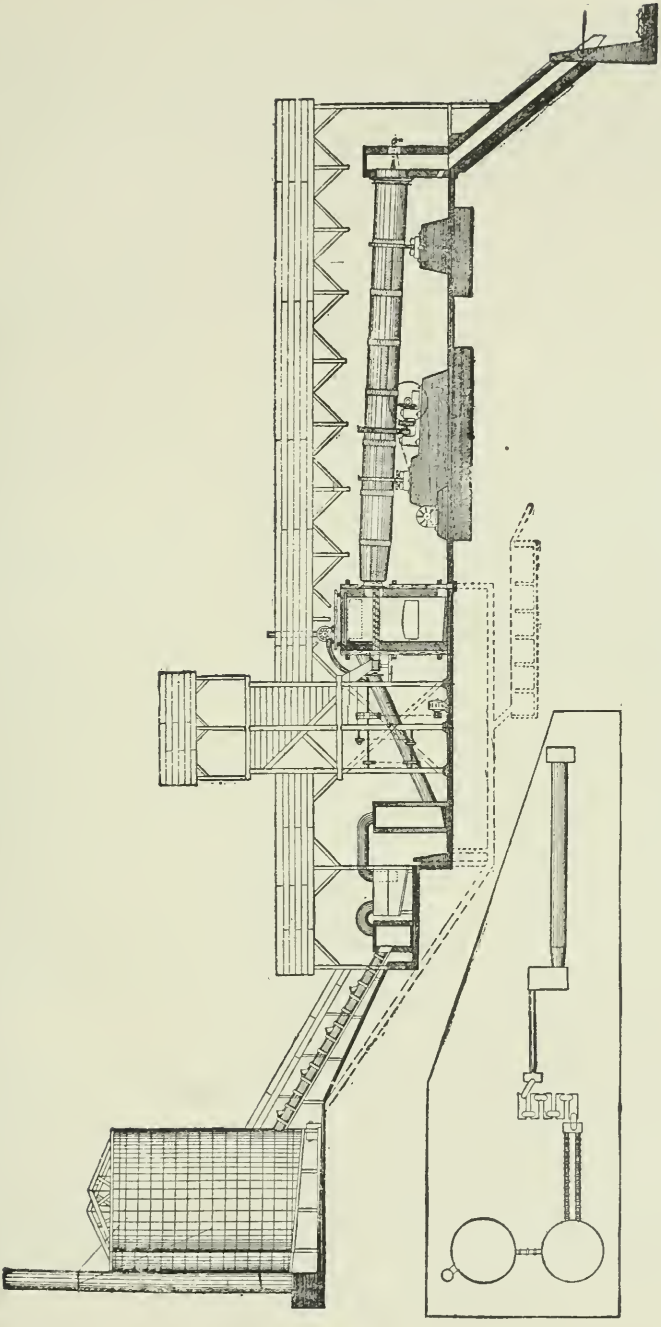

Fig. 171.—Rotary Furnace—New Idria Type.

It was proposed a few years ago to use the MacDougall type of hearth instead of the Scott furnace for the treatment of mercury ores, and particulars of a six-hearth Herreshoff roaster, at New Almaden, are given below.

Roasters of the MacDougall type are well adapted for the burning of high sulphur ores, or for ores that contain metallic mercury, which on this account cannot be roasted in any of the shaft furnaces. They are economical of fuel, and can be erected for about half the cost of the regular tile furnace. On the other hand, they require more highly skilled labour than the tile furnace, and the cost of maintenance and working is higher.

They have the advantage of being able to control the temperature on each hearth, and will find their greatest application in the smelting of large tonnages of cinnabar concentrate where the sulphur content is sufficiently high to reduce materially the amount of external fire necessary (*Landers*).*

" A Herreshoff furnace has been in operation at the New Almaden.† This furnace is 14 feet inside diameter, and has six hearths, plus a drying floor on the top. There are two fire-boxes on No. 5 hearth (next to bottom) level set opposite to each other. On No. 2 hearth level, about one-third of the way around from the top exit pipe, a third fire-box has been added, in order to keep the temperature of the gases above 315·6° C. while going through the Cottrell dust precipitator which follows. The central column and the rabble arms are air-cooled, the resulting hot air being utilized for concentrate drying and other purposes.

" A Brown recording pyrometer is connected in at the furnace exit for regulation of the fume temperature.

" This furnace is stated not to work economically on material coarser than $\frac{3}{4}$-inch.

" Up to 58 tons have been treated in 24 hours, but it seems to do its best work at between 40 and 50 tons. Feeding and discharging are both automatic.

" By reason of the dust raised as the ore is scraped from one hearth to the next, an accumulation of dust was obtained in the condensers. To correct this, a Cottrell fume precipitator was installed between the furnace and the first condenser. To prevent the mercury from condensing in the precipitator the temperature of the gases on leaving the furnace is kept above 315·6° C. Following the last condensing chamber is a second Cottrell precipitator, to throw down any remaining mercury ' mist ' in the fumes.

" The fuel consumption of this furnace is rather high, being approximately 8 gallons of oil per ton of ore treated, as against 5 to 6 gallons per ton for a 50-ton Scott furnace."

At Monte Amiata (Italy), as a preliminary to smelting, the ore reduced below 35 mm. size is dried in a special double-shaft furnace. The ore is filled in at the top and shot down between zig-zag iron plates. The heating channels are so arranged that the hot gases pass first over the damp ore. In order to prevent as far as possible the generation of dust, and to protect the men who attend the furnace against mercury poisoning, an automatic chain conveyor removes the dried ores from underneath the furnaces, and passes them on to a shaking screen of 35 mm. mesh. All the material which passes through this screen is conveyed for further treatment to Czermak-

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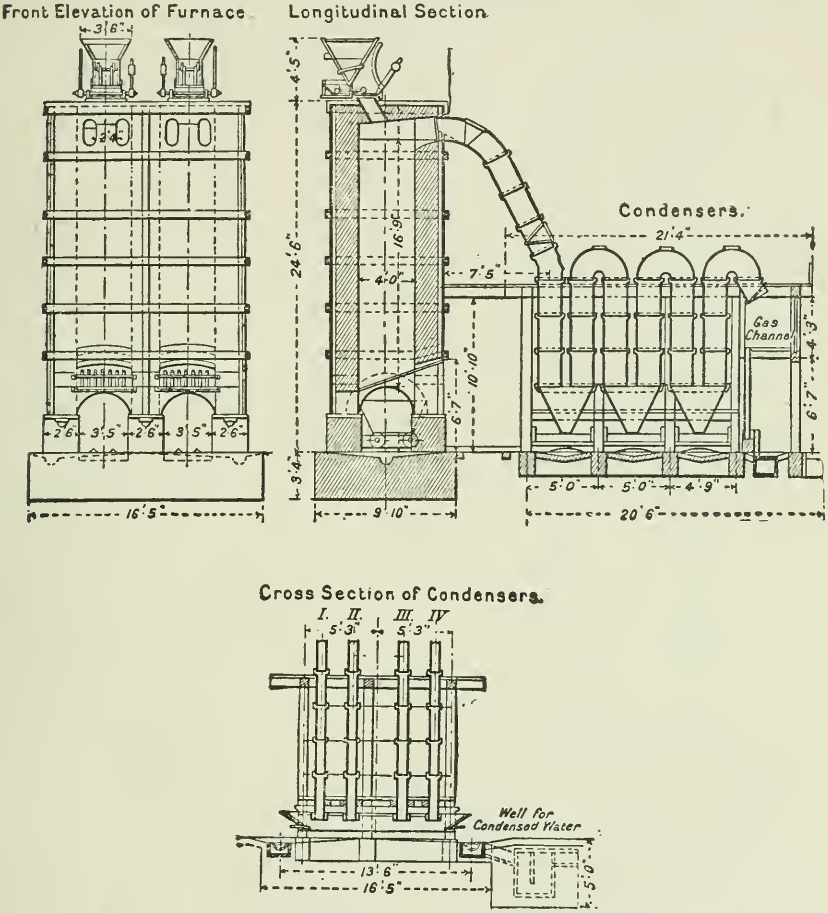
* Landers, *Eng. and Min. Journ.*, Oct. 1916.

† *Opus cit.*, pp. 250-252.

Spirek tile furnaces. This shaft furnace for drying the ores has proved a complete success. The pieces of ore over 35 mm. are roasted in an ordinary shaft furnace.*

The furnaces employed for the "air-reduction" process are of many kinds, although the general principles on which they are constructed are the same in all. Furnaces such as the Idrian, the Aludel, and other old types are


Front Elevation of Furnace
3' 6"
2' 4"
2' 6"
3' 5"
2' 6"
3' 5"
2' 6"
16' 5"
Longitudinal Section
4' 5"
24' 6"
3' 4"
16' 9"
4' 0"
7' 5"
10' 10"
6' 7"
9' 10"
Condensers.
21' 4"
Gas Channel
4' 3"
6' 7"
5' 0"
5' 0"
4' 9"
20' 6"
Cross Section of Condensers.
I.
II.
III.
IV
5' 3"
5' 3"
Well for Condensed Water
13' 6"
16' 5"
5' 0"

Figs. 172 and 173.—Czermak-Spirek Shaft Furnace and Condensers.

practically obsolete, and only of historical interest, a description of them will hence be unnecessary here. Only the most important modern furnaces, those which are in practical use at the present time, will, therefore, be dealt with.

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* *Min. Journ.*, March, 1912, p. 200.

Modern furnaces for the treatment of the usual ores are of two classes—shaft furnaces and reverberatory furnaces—the latter being employed to only a small extent. All are continuously working furnaces, whilst formerly all were intermittent.

The two classes may be subdivided, as follows :—

I. Shaft Furnaces.—1. Without inclined shelves. Used for large ore.

- (*a*) Spirek shaft furnace without external fire-places.
- (*b*) Novak ,, ,, ,,
- (*c*) Exeli type of shaft furnace with external fire-places.

2. With inclined shelves. Used for large medium and fine ore.

- (*a*) Scott furnace.
- (*b*) Litchfield furnace.

Intermediate between this and the following class there is the very important *Czermak-Spirek Schüttröstofen*, termed also *four à cascade* and "*tile*" *furnace*, with ridges, which may be considered either as a group of low-shaft furnaces or as a multiple-hearth reverberatory furnace. It is suitable for medium and fine ores.

II. Reverberatory Furnaces.—Spirek-Czermak reverberatory furnace, without ridges, suitable for small ores which form much dust, for ores which decrepitate, and for residues from the treatment of mercurial soot.

In addition to the furnaces of the above classes, there are also :—

Retort furnaces which, however, are only suitable for very rich ores, concentrates, and mercurial soot, and their use is, as a rule, confined to the treatment of the two last-named classes of materials.

Shaft Furnaces without Inclined Shelves.

The Spirek shaft furnace is the most modern of this class of furnaces, and is displacing or has already displaced the Novak furnace, as this had in several works displaced the Exeli.

The Spirek Shaft Furnace (Figs. 172 and 173) * consists of a square shaft of ordinary fire-brick braced with angle iron and tie-rods, and supported on columns. Its usual dimensions for an output of 6 to 7½ tons per day are about 4 feet by 6 feet in cross-section, and 16 feet 9 inches in height internally from the bottom discharge plates to the outlet for the vapours.

The bottom of the furnace is placed at a height of about 5 feet above the floor line, so that a truck can be run under it to receive the spent ore. The outlet pipes by which the mercurial vapours are led to the condensers are at one side of the shaft immediately below the top. The bottom consists of sloping iron bars and plates, which can be moved when the spent ore has to be discharged.

Iron plates below the columns and a dished floor of concrete prevent loss of mercury in the ground. The furnaces are generally built in pairs, as shown in the figures.

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* *Min. Ind.*, vol. x., pp. 559-561.

The charge consists of ore varying in size from $1\frac{1}{4}$ inches up to $7\frac{1}{2}$ inches, and about 2 per cent. of charcoal. A pair of furnaces of the dimensions given will treat from 12 to 15 tons of ore in twenty-four hours. The cost of working those furnaces is said to be so small that ores containing only 0·01 per cent. of mercury can be treated profitably.*

The condensers employed are described on p. 449, *et seq.*

The Novak Shaft Furnace was until recently a favourite furnace for the treatment of coarse ores of 0·3 per cent. Hg and over, and of about $\frac{3}{4}$ mesh size and upwards, and although it is being displaced by the above furnace, it is still in use in some works.

The Novak furnace is a simple shaft furnace, rectangular in section, measuring about 8 feet by 6 feet 6 inches at its broadest part, and about 31 feet in total height (Fig. 174).

It has two openings on each side of the bottom of the shaft for the discharge of spent ore. Running across the bottom is a roof-shaped ridge of cast iron perforated with numerous holes, through which air is admitted to the furnace. The furnace is charged by means of a cup and cone, which is covered at the top with an iron cover, fitting into a water-jointed groove. These furnaces are sometimes built in blocks of three.

The mercury vapour and gases pass away to the condensers through an iron pipe in the side of the furnace near the charging hopper.

About 12 tons of ore can be treated in a furnace of the above dimensions in twenty-four hours.

The fuel is charcoal, which is mixed with the ore before charging.

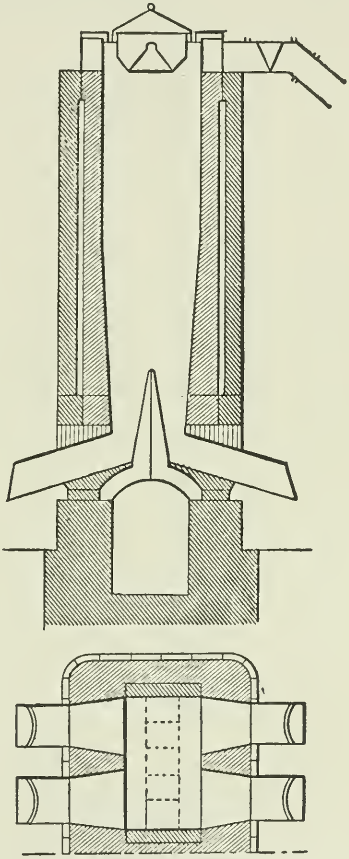

Fig. 174.—Novak Shaft Furnace.

The Exeli Furnace.—From what has already been said regarding the disuse of this furnace, only a brief notice of it is necessary. It is a shaft furnace, circular in section, the heat for the reduction of the ore being supplied by three external fire-places. The internal dimensions of those at New Almaden (California), where two were employed in 1903, were—height to the outlet tube 17 feet, diameter of the shaft above the fire-places 5 feet 6 inches, diameter at base 3 feet 9 inches. Each treated 12 tons of ore in twenty-four hours, using wood as fuel. Lignite or coal can also be used.

The spent ore is discharged through three openings below the fire-places.

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* *Min. Ind.*, vol. x., pp. 559-561.

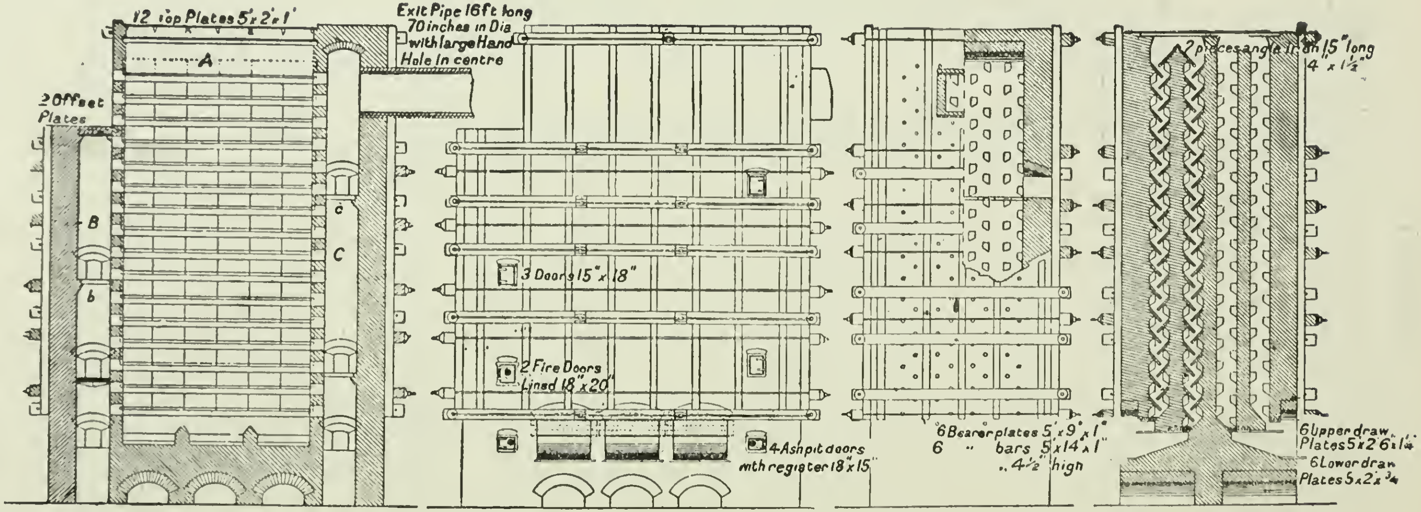
12 Top Plates 5'x 2'x 1'
A
2 Offset Plates
B
b
c
C
Exit Pipe 16ft long 70 inches in Dia with large Hand Hole in centre
3 Doors 15" x 18"
2 Fire Doors Lined 18" x 20"
4 Ashpit doors with register 18" x 15"
6 Bearer plates 5' x 9" x 1"
6 " bars 5' x 14" x 1"
" 4½" high
2 pieces angle iron 15" long 4" x 1½"
6 Upper draw Plates 5 x 2' 6 x 1¼
6 Lower draw Plates 5 x 2' x ¾

Fig. 175.—Hüttner and Scott's Furnace. (Bulletin No. 27, *The Quicksilver Resources of California*, issued by the California State Mining Bureau, 1903.)

Shaft Furnaces with Inclined Shelves.—These furnaces are practically in universal use in America for coarse, medium, and even fine ores. The chief type is the *Scott furnace* or its modifications; in fact, almost the whole production of mercury in California in 1910 and all in Texas was from these furnaces. They range in capacity from 10 to 50 tons in twenty-four hours.

The Scott Furnace (Fig. 175).—This furnace consists of four rectangular ore chambers or shafts built in one block with a fire-place common to all. In some of the larger furnaces there are two fire-places. In each shaft from eight to sixteen series of tiles are fixed, as shown in the figure, the two upper rows being of cast iron, and the others of fire-clay.

The tiles are supported at the top by projections from the side walls, and at the bottom by fire-bricks resting in depressions on the tile below. They are placed at an angle of 45°. For ordinary coarse ore the openings between them, through which the ore falls, are 8 inches, and for fine ore 3 inches wide. The shafts or ore chambers are of various sizes, ranging from 8 feet 9 inches to 11 feet 6 inches in length, 18 inches to 25 inches in breadth, and 27 feet 3 inches to 30 feet 9 inches in height from the roof to the point of discharge.

At one end of the four shafts there is the fire chamber, containing the fire-place, and at the opposite end the vapour chambers. The fire-grate runs from one side of the block to the other, and is stoked from both ends. The fuel used is generally wood, but oil has been introduced at New Almaden (California), and wood and gas in a modified form of furnace in Oregon.

The partition walls between the fire chamber and the ore chambers and between the ore chambers and the vapour chamber are pierced with pigeon holes, through which the flame and gases from the fire-place pass.

The gases from the fire-place and the necessary air for the reduction of the ore are made to traverse the ore chamber in a zig-zag manner by the partitions *b* and *c* in the fire chamber B and the vapour chamber C respectively. Thus, by *b* they are made to pass through the lower third of the ore chamber to C, up which they cannot rise, owing to the partition *c*, but must return to B through the next third of the ore chamber. The gases then traverse the remaining part of the ore chamber, and carrying the mercury vapour, pass out of the furnace through the exit pipe, and thence to the condensing plant.

Though operators may differ as to the degree of drying necessary before charging the ore to the Scott furnace, all are agreed that it is poor policy to feed wet ore.

The ore, which is fed in through hoppers at the top of the ore chambers, slides down from one tile to another until it reaches the discharge openings at the bottom. In case there should be any obstruction to the passing down of the ore, peepholes, made of 3-inch gas pipe, are arranged in the end walls, through which iron bars can be inserted to remove it. These holes are closed with clay plugs during the working of the furnace. The spent ore is discharged through double doors, on each side of the furnace, about every forty minutes, when an equivalent quantity of fresh ore is charged in.

The output varies from 18 to 36 tons in twenty-four hours, according to the size of the furnace and the nature of the ore. At the Boston and New Idria Mines (California) 60-ton furnaces are in use.

The furnace block is best enclosed in iron plates, but in many cases they are only surrounded by a wooden framework strengthened with iron tie-rods. The average percentage of mercury in the ores treated in these furnaces in California in 1910 was 0·6, and in Texas 1·5.

The question of temperature control is most important in the operation of such furnaces as the Scott, the efficient control resulting in fuel economy; safer and more certain furnace operations are also gained by this means. "A suitable installation for this purpose consists of an indicating pyrometer, situated near the furnace for the use of the furnacemen, a recorder in the superintendent's office or at other convenient point, and perferably at least two thermo-couples in each furnace" (*Duschak*).*

The Litchfield furnace, which is a modification of the Scott furnace, and is in use at the Great Western Mine, Lake County (California), has a fire chamber on each side of the ore chamber, and the tiles in the latter are arranged as shown in Fig. 176. The fuel used is oil. There are two furnaces, one for fine ore with a capacity of 30 tons per day, and one for coarse ore treating 12 tons.

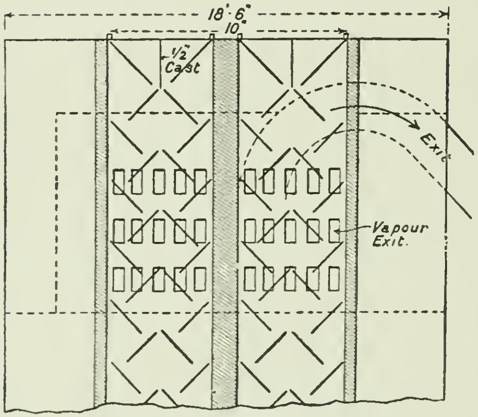

Fig. 176.—Arrangement of Tiles. Litchfield Furnace.

The Czermak-Spirek Shelf or Tile Furnace (Four à Cascade), Fig. 177.—This furnace is of a type intermediate between shaft furnaces and reverberatory furnaces proper, and, as has been already stated, may be considered either as a multiple hearth reverberatory or as a group of low shafts. It is in general use for small ore in all the chief works in Spain, Austria, Italy, and Russia.

It consists of four rectangular chambers or low shafts built in one block. At each short side of the block is a main fire-place, and in each long side a subsidiary fire-place, by which the chambers are heated. The whole stands in a shallow dish of iron plates, riveted together to catch any mercury which may escape, and supported by columns. The furnace should be entirely open to observation both at the sides and below.

In each chamber are fixed four to eight rows of ridges, having the form and arrangement shown in the figure, so that the ore charged in gradually passes down from one to the other until it reaches the discharge opening, when it should be free from mercury.

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* *Opus cit.*, p. 239.

The uppermost ridges are of cast iron, the others of fire-clay. The width of the openings through which the ore falls between the ridges varies at different works, and even in different furnaces in the same works, according

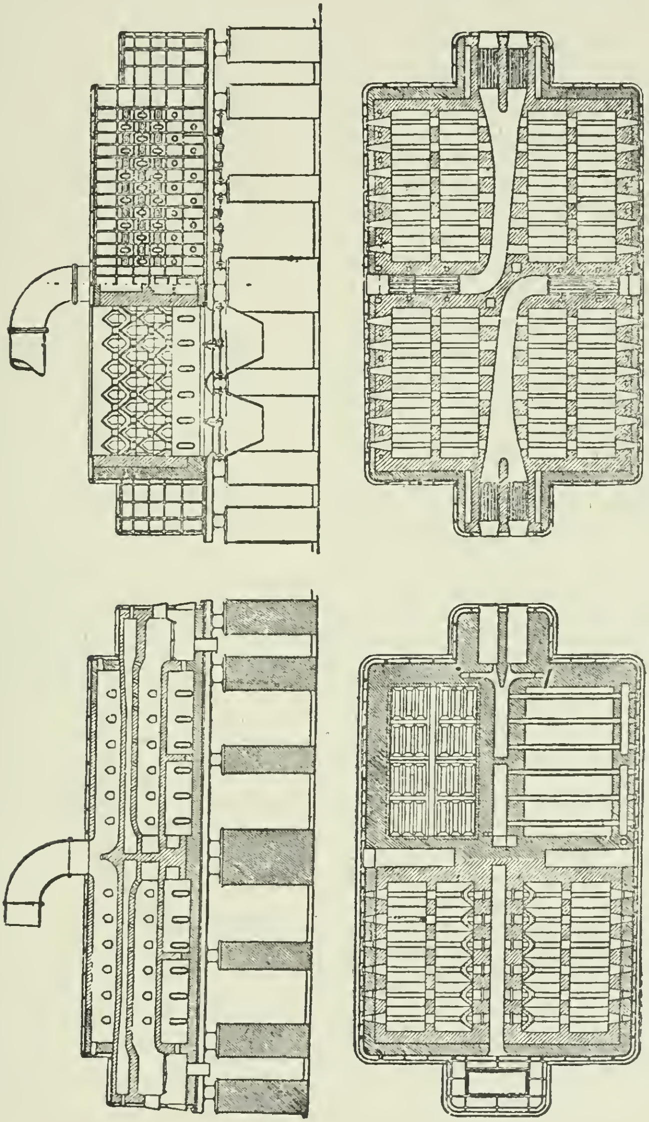

Fig. 177.—Czermak-Spirek Tile Furnace. (Borchers, *Hüttenwesen*, p. 42.)

to the size and richness of the ore; generally it ranges from about 3 inches to $4\frac{3}{4}$ inches.

The flames and hot gases from the fire-places mix in the channel in the middle of the furnace which connects the two main fire-places, and serves as a combustion chamber. They then pass below the lowest row of ridges, and circulate backwards and forwards through the empty spaces below the others, finally passing out through the outlet tube leading to the condensers, carrying the mercury vapour with them.

The ridges and the ore upon them are thus heated to the temperature necessary for the reduction of the cinnabar.

The air for the combustion of the fuel and the oxidation of the sulphur of the cinnabar is heated in elliptical cast-iron tubes, which traverse the space below the lowest row of tiles, into which the spent ore falls. The spent ore is also thus cooled, it is said, to below 100° C.

In the large furnaces the temperature in the combustion chamber reaches 700° to 800° C., and about 400° on the upper rows of tiles.

The ore is charged through openings in the top of the chambers containing the uppermost ridges of tiles, where the ore is dried, and to prevent the escape of mercury vapour the bed of ore is kept about 2 feet in thickness above each opening. Also to prevent the escape of the vapour, a slight vacuum is kept within the furnace.

The spent ore is discharged about every two hours, and falls into the vaults below the furnace, from which it is sluiced out by water. An equivalent amount of raw ore is then charged in. There are peepholes in the long sides of the furnace for observing the progress of the operation, and for the introduction of bars when required to assist the descent of the ore. The fuel used is either wood, lignite, or coal. The output of a given furnace varies considerably, according to the size and reducibility of the ore.

Generally the furnaces for the treatment of the ordinary ores have a capacity of from 12 to 24 tons in twenty-four hours. Smaller furnaces are, however, in use for richer ores and materials. The condensers usually employed with these furnaces in Europe are described on pp. 449 to 452.

In the Monte Amiata (Italy) district there have been fifteen of these furnaces. Of these seven had a capacity of from about 24 to 30 tons per day, four from 12 to 15 tons, and four from 2 to 8 tons, all using wood as fuel.

Reverberatory Furnaces.

The use of reverberatory furnaces is almost entirely, if not entirely, restricted to Europe, and even there they are but little employed, as in every way they are inferior to the furnaces just described for the treatment of ordinary ore, on account of the cost of fuel and labour and greater loss of mercury. As already pointed out, however, when ores of moderate richness are very dusty, or decrepitate in other furnaces, they may be required, also for the treatment of the mercurial residue obtained from "stupp," and it is only for such that they are used. There are several kinds, but the most efficient is the following, which was designed by Czermak and modified by Spirek.

Czermak-Spirek Reverberatory Furnace (Fig. 178).—This is a long reverberatory furnace with a bed or hearth having below it a series of parallel flues leading from the fire-place. The flame and gases from the fire pass through these flues, and then over the hearth, thus heating it and the ore. The gases then pass out of the furnace together with the mercurial vapours through two outlet tubes, by which they are led to the condensers.

The hearth, which is constructed of fire-clay tiles, is 18 feet long and 7 feet 8 inches broad. There are two working doors on one side of the hearth. The ore is charged in through a hopper near the front end of the furnace, and the spent ore is discharged through a door into a receptacle. The furnaces are built in pairs. They stand in a shallow pan of wrought-iron riveted plates, resting on old rails, and supported above the ground by brick columns. The output is small, being only from about 6½ to 7 tons in twenty-four hours.

Retort Furnaces.—These furnaces, although in extensive use for the distillation of amalgam at gold and silver mines, can only be used for very high-grade ores and concentrates and products rich in mercury.

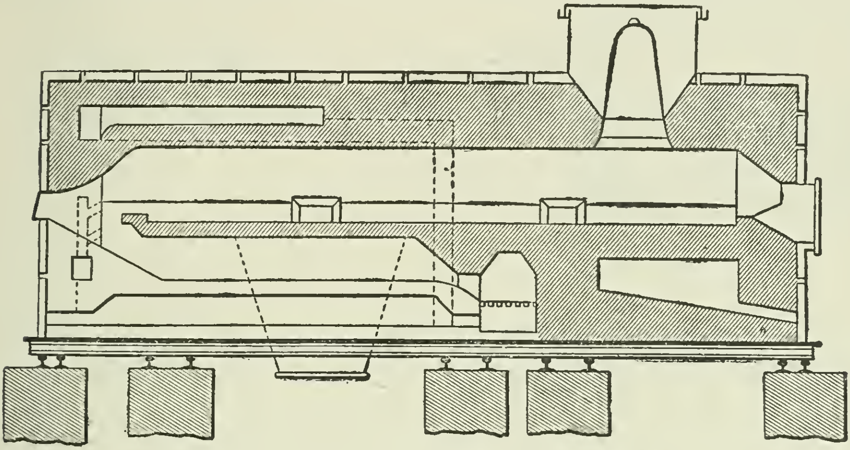

Fig. 178.—Reverberatory Furnace for Mercury Ores.

Except in one or two places in California and in Nevada, they are not employed anywhere on account of their small capacity and high cost of labour and fuel. On the other hand, as the mercury vapour is not diluted or contaminated with the products of combustion of the fuel, it is readily condensed.

The following account and the illustrations of these furnaces, as employed at the Manzanita Mine (California) are taken from Bulletin No. 27, "The Quicksilver Resources of California," issued by the California State Mining Bureau, 1903.

The ores are rarely of sufficiently high grade for the process, and are hence concentrated by a series of washing processes, the disadvantages of which have already been pointed out. When the amount of iron pyrites present is small the concentration attained is about 20 to 1. The retorts are of cast iron, circular in section, and vary in length from 7 to 9 feet, and in diameter from 10 to 12 inches. Semi-circular or ⌓-shaped retorts, 18 inches wide and 12 inches high are also employed.

The retort furnace at Manzanita is shown in Fig. 179, also a section through the furnace and one of the retorts.

The furnace consists of a row of ten retorts set in brickwork, with a fireplace at one end of the row. Each retort is fitted with a water-jacketed tube resembling a Liebig's condenser for the condensation of the mercury. The door closing each retort is set well within it, in a line with the inside of the furnace wall, to guard against the cooling of the part of the retort outside the heating chamber and consequent accumulation of mercury there.

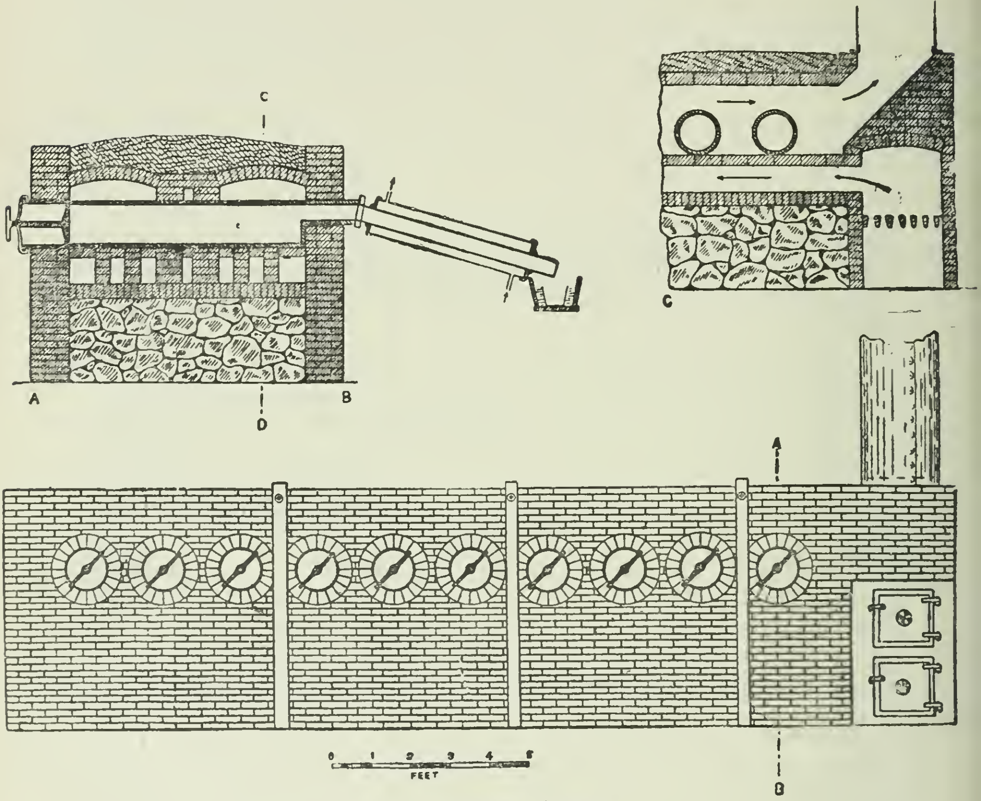

Fig. 179.—Retort Furnace.

The charge consists of about 150 lbs. of the dressed and dried ore mixed with the necessary proportions of lime, and should fill only about one-third of the retort. The reaction which occurs is as follows :—

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4.$$

The retorts are kept at a relatively low temperature from 375° to 400° C., and about twelve hours are required for working off a charge.

The Equipment of a Works.—According to Spirek, the furnace equipment of a typical works in Europe for the treatment of 45 tons of ordinary ore with an average content of about 1·2 per cent. of mercury per day would be as follows:—*

1 large Czermak-Spirek tile furnace (four à cascade),	16 tons.
1 medium ,, ,,	8 ,,
1 small ,, ,,	2 ,,
3 shaft furnaces, Czermak-Spirek,	18 ,,
1 muffle furnace,	1 ,,

The Condensation of Mercury.—As mercury condenses at 360° C., it might be thought that its condensation would present no serious difficulties, neither are any encountered when its vapour is concentrated, as in the retorting of gold or silver amalgams.

In the treatment of ordinary ores, which contain for the most part less than 1·0 per cent. of mercury, the products of distillation consist, however, of large volumes of gases from the fuel and the decomposition of the ore, together with steam and air, with but a very small proportion of mercury vapour, the condensation of the metal without undue loss is, therefore, by no means an easy matter.

The gaseous products issuing from the furnaces in which the ore is treated, and which have to be condensed, are—mercury, steam, mercurial salts, and sulphuric acid, associated with air, sulphur dioxide, carbon dioxide, hydrocarbon compounds, particles of ore, and ash and soot from the fuel. It is obvious, therefore, that the appliances for the condensation and collection of the small amount of mercury they contain must be very capacious, or have a large area of cooling surface.

Their capacity must be sufficiently great on account of (*a*) the volume of the gases, and (*b*) the slow rate at which these gases must traverse the condensing system, in order to allow sufficient time for the greatly diluted mercury vapour to condense and settle.

In Europe the condensing plant in the most important works usually consists of a series of tubes, of sufficient cross-section not to impede the passage of the vapour, made generally of stoneware, followed by one or more chambers constructed of wood and glass.

In America tubes are rarely employed, the condensers in common use being a succession of chambers of brickwork, sometimes followed by towers of wood and glass. Wooden condensers, either vertical or horizontal, are now being used to a considerable extent, and have been found satisfactory where the temperature of the gases permits their use.

In both systems the gases are drawn through by fans, which also enable the pressure within the furnaces and the condensing plant to be kept slightly below that of the atmosphere, thus preventing any escape of mercury vapour from the plant. Chimney stacks, sometimes specially heated, were formerly employed, but these have been given up at most works, on account of the difficulty experienced in maintaining with them a uniform depression within the apparatus. Care, of course, must be taken that the depression is small, or the flow of the gases will be unduly accelerated. It may be mentioned here that even with the best modern systems of condensation a small percentage of mercury still escapes, and is lost.

The Cottrell system of electrical precipitation offers a highly efficient means for collecting the mercury existing in finely divided particles as mist in the fume, after the larger particles have been retained in the condensers.

* *Min. Ind.*, 1898, p. 581.

The materials which can be used in the construction of condensers should possess, as far as possible, the following characters :—

(*a*) Resistance to the action of the acid vapours.
(*b*) Resistance to the absorption of mercury.
(*c*) Be good conductors of heat.

None of them, however, perfectly fulfils all these conditions.

The materials used are :—

1. *Stoneware.*—When this material is properly made, and where the temperature permits of its employment for cooling and condensing pipes, it is unsurpassed by any other.

2. *Iron.*—Cast iron is extremely serviceable in those parts of the condensers where the temperature is sufficiently high to prevent the condensation of the acid vapours, as it is a good conductor of heat, and rapidly cools the gases. On the other hand, in the cooler parts, it is rapidly attacked by these vapours, although this may be prevented to a considerable extent by coating it with cement, or where the temperature is sufficiently low with a mixture of asphalt and coal tar.

3. *Brickwork.*—Bricks and the mortar joints are very liable to be disintegrated by the acid vapours. In America, where brickwork condensers are in extensive use, this has been very considerably mitigated by the use of dry-pressed machine-made bricks and extra close mortar joints. At some works, with the same end in view, the brickwork is coated with cement in the hotter and with asphalt in the cooler condensing chambers.

4. *Glass and Wood.*—Condensing towers and chambers for the cooler vapours at the end of the condensing system are sometimes constructed entirely of wood and glass, and as long as they can be kept continuously at work are satisfactory, but when a stoppage occurs they soon become leaky from the warping of the wood.

5. *Wood.*—The final condensing chambers sometimes called "dust chambers" are generally made of wood in Europe, and at some works the woodwork receives a coating of paraffin or of asphalt and coal tar, to prevent absorption of mercury.

Lately, wood has been adopted for the construction of condensers at the Oceanic mine, the New Idria mine, the Aetna mine, and at the Cloverdale mine. At New Idria the round form is being adopted, while at the other three they are built rectangular.

The Condensers.—The condensers are of very varied forms and arrangement. The older forms are, like the old furnaces, merely of historical interest, hence only those which are regarded as the most efficient types, and which are now in actual use at the chief centres of the production of mercury, will be dealt with.

Before describing them in detail, it will be well to consider first the conditions which a good condenser must satisfy. They are, according to Spirek :—*

1. The gases after leaving the furnace must be cooled quickly below 100° C.

2. The water used for cooling must be kept separate from that used for condensation, in order not to have too much motion in the collecting tanks for the mercury and mercury-bearing soot (stupp), by which some of the metal might be lost.

3. All the openings in the condenser must be water-sealed.

4. The mercury must be caught and retained beneath the surface of water.

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* *Min. Ind.* (1898), vol. vi., p. 570.

To these may be added :—

5. Every part must be readily accessible.

The condenser designed by Czermak satisfies these conditions, and is the type on which all the tube forms of condensing plant are based.

The Czermak Condenser.—This condenser in its simplest form is shown in Fig. 173. It consists of a series of pairs of vertical tubes of cast iron or glazed stoneware of elliptical cross-section set in a line. Of these lines there may be six or nine, according to the output of the furnace.

Each pair is cemented at their bottom ends into a V-shaped receiver, the lower end of which is open, and dips to a depth of about 2 inches into water, contained in an iron tank, in which the mercury and mercurial soot (stupp) collect. Each pair is also connected with the next by a cap-piece containing a manhole.

The straight part of each tube is about 8 feet in length and 20 to 24 inches in long diameter. The tubes are supported by a wooden framework, and are cooled by water.

Although iron is a much better conductor of heat than stoneware, iron tubes have been given up in some works, at all events for the cooler parts of the condensers, on account of their rapid destruction by the acids in the vapours. The gases and vapours are led from the furnace to the condensers by iron pipes, and after traversing the condensers enter a large wooden condensing chamber, divided by baffle walls, in which they follow a zig-zag course, and then pass out to a fan, and thence to the chimney stack. The temperature is noted from time to time daily by thermometers, and the vacuum by alcohol manometers, placed in several parts of the plant.

The condensing or dust chamber, as it is sometimes called, is built on columns, and has a cement floor sloping to a gutter, by which any free mercury flows out to a collecting pan. In some works the first series of tubes is followed by a wooden dust chamber, after which there is a second series of tubes, and finally another wooden chamber. The entire floor of the condensing plant has a cement floor, with channels to catch any mercury that may escape from the apparatus, and sometimes a wooden floor above it.

After every five or ten days, according to the richness of the ore, there is a "clean up" of the series of tubes. This is effected by first closing the entrance and exit valves of half the condensers, then removing the covers from the manholes and cleaning the tubes with scrapers and brushes and a jet of water.

The solid particles of soot, ore, and ashes which are carried over in the gases collect on the sides of the tubes and in the iron pans mixed with mercury forming the material called stupp or soot. This is very rich in mercury, and in the treatment of very poor ores all or nearly all the mercury will be contained in it.

With ordinary ores, according to the percentage of mercury present in them, a greater or less amount of the metal will be obtained free in the iron tanks, and the quantity of stupp will be proportionately reduced.

The following advantages are claimed for this form of condensing plant :—

(1) Slow circulation of gases in the condensers, less than 2 feet per minute, allowing time for solid materials to deposit.

(2) The temperature of the gases in the condensers is kept low, between 20° and 30° C., water being used for cooling.

(3) All the gas pipes which communicate with the collecting troughs are kept under water seal.

At a condensing plant in Idria, arranged for a Czermak-Spirek tile furnace, the condensers, which are of the Czermak type, are set in three groups of three rows each, the gases and vapours from the furnace being led to the condensers by means of a large cast-iron tube, which at its further end rests on a brick column. Here it enters a cast-iron box or distributor, in the opposite side of which there are three openings. In each of these openings a pipe is fitted to connect with the condensers.

Near the condensers each of these pipes enters a similar box to that just described, from which three pipes issue, each of which leads direct to a row of condensers. The condensers consist of vertical pipes of glazed stoneware, elliptical in cross-section, as described above. At the further end of each row of condensers a pipe from the last and shorter tube conducts the gases to a wooden condensing chamber containing the usual baffle walls.

American Condensing Plant.—In America the condensing plant consists almost exclusively of a series of chambers built of brickwork, supplemented at one or two works with towers constructed of wood and glass. In 1910 over 95 per cent. of the mercury produced on the Pacific Coast was condensed in brick chambers. For a new arrangement, see p. 436.

The chambers vary considerably in dimensions, those built by Scott a few years ago are 14 feet 6 inches by 8 feet 6 inches inside, and 22 feet high from the lower part of the floor to the roof, and have 9-inch walls. At the Oceanic Mine (California) they are 16 feet by 8 feet, and 29 feet high. Each is divided longitudinally into two compartments by a partition wall, as shown in Fig. 180. The floor of each chamber is coated with cement, and slopes towards a gutter in the middle and towards the ends for the discharge of the condensed mercury.

There are two rows of openings in the side walls for the convenience of the clean up. The top of each compartment is closed by an arch, but in some cases by iron plates to aid the cooling. In some plants to further accelerate the cooling and condensation of the vapours, narrow iron tanks, called "waterbacks," through which water is circulated, are built into the walls, especially in the end walls of the first and second chambers. The walls of the further and cooler chambers are coated with asphalt and coal-tar mixture.

The connections between the furnace and the first chamber, and between this and the next are made with iron pipes; the others are connected with earthenware pipes. Two chambers are often built in one block, but separated by an intervening space of 4 feet for cooling purposes.

In a condensing plant erected in Texas, the first four condensers are built of dry-pressed machine-made bricks, of special quality, the bricks being laid with very close joints, thus presenting a smooth surface, which prevents to a great extent the absorption of mercury and the adherence of soot. Every condenser is also covered by a roof, whereby it has been found possible to keep them at a steady temperature, even during extremely hot weather.*

The number of these chambers in a condensing system depends, not only on the capacity of the reduction furnaces, but also on the grade of the ore, the vapours from poor ores requiring a larger space than those from rich ores.

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* *Eng. and Min. Journ.*, Dec. 1906.

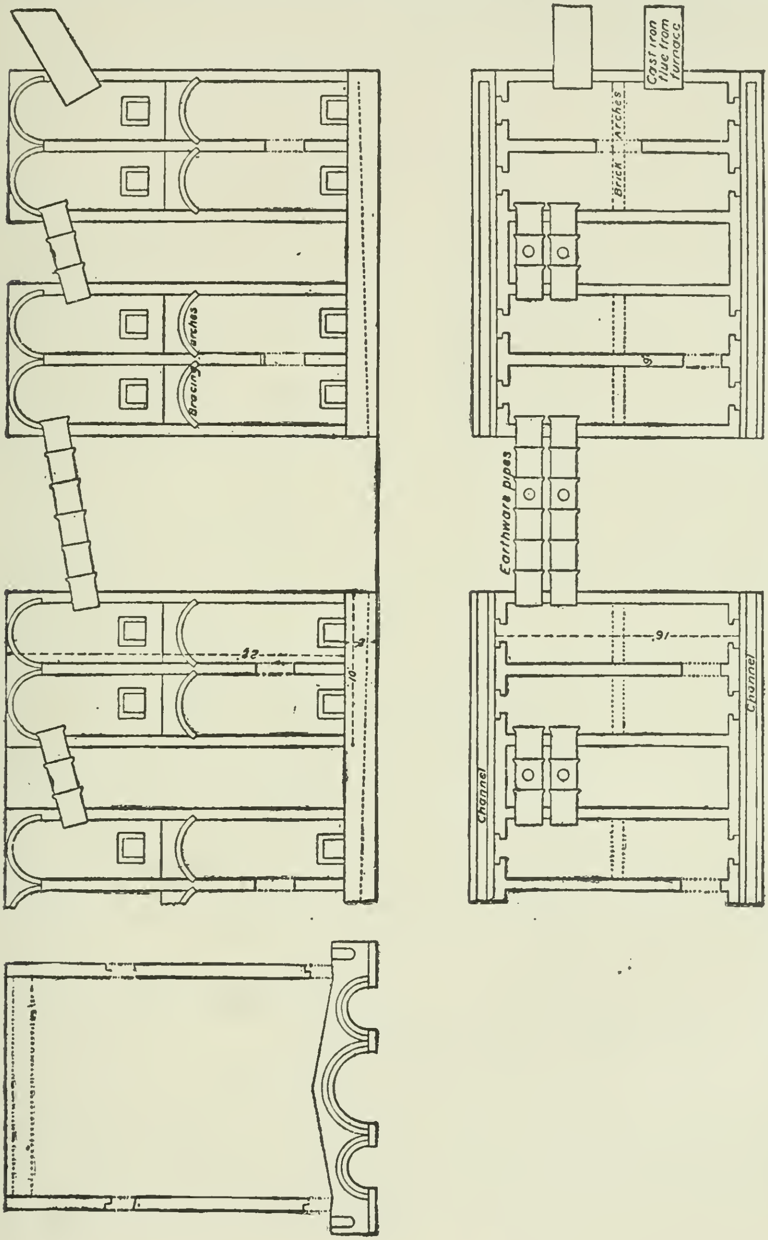
Cast iron flue from furnace
Brick arches
Bracing arches
Earthware pipes
Channel
Channel
32
10
8
9
91

Fig. 180.—Scott's Brick Condenser Plant. (Bulletin No. 27, California State Mining Bureau.)

Scott considers that the condensing room required for a 40-ton furnace treating the ordinary run of Californian ore should be 17,000 cubic feet, and for a 50-ton furnace 20,000 cubic feet.

The brick condensers are supplemented in a few works by towers of glass in a wooden framework, and in some by the old so-called "water tank" condenser. The glass towers have been given up in several plants. They were usually about 4 feet by 4 feet in cross-section, and 25 feet high.

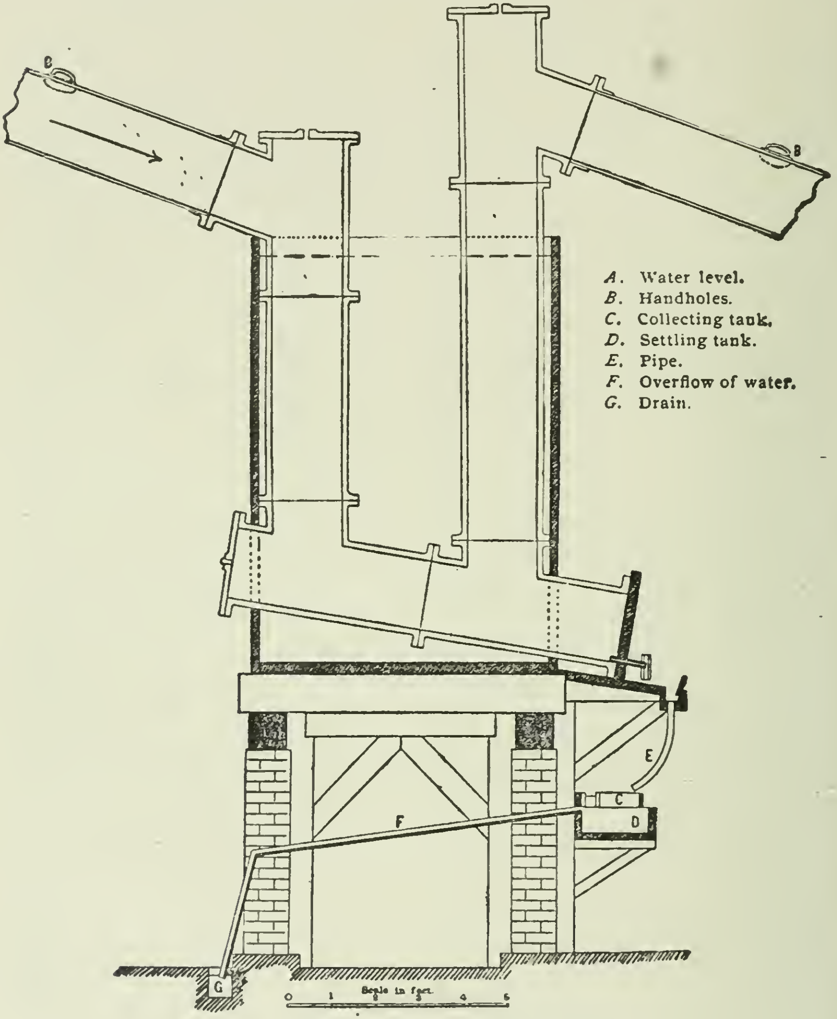
B
B
A. Water level.
B. Handholes.
C. Collecting tank.
D. Settling tank.
E. Pipe.
F. Overflow of water.
G. Drain.
E
C
D
F
G
0 1 2 3 4 5
Scale in feet.

Fig. 181.—Water Tank Condenser.

At Almaden (Spain) the brick condensers are followed by glass chambers.

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* *Ibid.*

In each chamber there are three baffle walls, with openings arranged so as to cause the gases to take a zig-zag course.

The old "water-tank" condenser is illustrated in Fig. 181, which is self-explanatory. It is in use in the important works at New Almaden (Cal.), where the tubes are about 22 inches in diameter.

Products of the Extraction of Mercury by the Air-Reduction or Roasting Process.—The products are :—

1. Fluid mercury.
2. Mercurial soot (stupp).
3. Residue.

1. The *fluid mercury* from the condensers is collected in receptacles, and sent to the weighing and bottling rooms, where it is filtered through canvas and transferred to wrought-iron bottles, called flasks, closed by screw plugs. Each flask contains 75 lbs. of mercury. The yield of fluid metal varies greatly, and is dependent on the grade and character of the ore and the nature of the fuel, whether wood or oil. The lower the grade of ore the less the production of free metal and the greater the production of stupp.

In California it is claimed that at some mines 70 per cent. or more of the mercury runs out of the condensers, but this can only be in exceptional cases. In Texas, according to Dennis (*Min. and Sc. Press*, Dec. 1909), with 1 per cent. ore, the free metal amounted to 46 per cent., and with 0·5 per cent. ore it was only 15 per cent.

According to Feust, of New Almaden (*op. cit.*), only from 3 to 4 per cent. of fluid mercury was obtained from the condensers when treating ore of 0·2 to 0·3 per cent. grade. The remainder of the mercury produced is obtained by treatment of the stupp.

2. *The stupp* consists of more or less finely divided mercury mixed with mercurial salts, dust ore, ash, and tarry hydrocarbons from the fuel, and material scraped from the sides of the condensers at the clean up. It always contains considerable quantities of mercury in the metallic state, sometimes amounting to 80 per cent., and the greater proportion of which can be extracted from it by simple mechanical treatment.

At the smaller mines in California the stupp is placed on a floor of asphalt or concrete, 8 or 9 feet wide and 12 feet or more long, of the form of a broad, shallow V-shaped trough inclined from the head to the discharge. It is mixed with lime or wood ashes to dry it, and worked about with hoes to cause the mercury to separate and run down into a receptacle at the lower end of the trough. The residue, which may still contain 10 to 30 per cent. of mercury, is treated either in a reverberatory furnace or a small Czermak-Spirek tile furnace, or sometimes in a retort.

At the larger mines in California and in Europe the stupp is treated in mechanical extractors of various forms, a method which is more effective, and superior in every way to the above. A typical machine consists of an iron pan about 3 feet 6 inches to 4 feet in diameter, with a shallow conical bottom and perpendicular sides. Its depth is about 2 feet. A central axle carrying four arms, set with stirrers resembling knives, and driven by bevel gearing, revolves in the pan. The bottom of the pan also has set in it a series of upright knives, and is pierced with 20 to 30 small holes, through which the disengaged mercury can escape.

The stupp is charged into the pan together with the necessary quantity of lime, the stirrers are set in motion, and the mass violently agitated. By this means the mercury unites in large globules, and runs through the holes in the bottom of the pan into a receiver placed below. The agitation is continued as long as any mercury separates. The residue is treated as described above.

3. The *residue* from the furnaces contains only such a very small proportion of mercury, little more than traces, when the operation has been properly conducted, that it can be thrown away.

When rich ores, concentrates, or residues are treated in retorts with lime or iron nearly the whole of the mercury is obtained as fluid metal, but generally some remains in the residue sufficient to pay for its treatment in the furnaces for poor ores.

Losses in the Extraction of Mercury.—The losses of mercury are due to several causes, the chief being imperfect condensation, leakage from the furnaces and condensers, and absorption in the materials of which the condensers are constructed. The last does not, however, represent total loss, as the absorbed metal is recovered when the apparatus is taken down for reconstruction, so that it means only locked-up capital plus the cost of recovering the metal.

Imperfect condensation can be remedied or diminished by having condensers possessing sufficient capacity and cooling area, and by keeping the temperature within them as low as is practicable.

Loss by leakage of vapour or metal may be reduced to a minimum by keeping the pressure within the condensers and furnaces below that of the atmosphere, by enclosing the furnaces in iron plates, and by having the whole plant arranged so that it is open to observation on all sides and below, and by providing impervious cement floors throughout the works.

The average amount of mercury lost is difficult to ascertain; in fact, in most works there are no means of determining it accurately. According to Spirek (*opus cit.*), it amounts to from 4 to 5 per cent. when Czermak-Spirek tile furnaces and Czermak condensers are employed—*i.e.*, after the condensing apparatus is impregnated with mercury. Dennis " guesses " the loss at about 5 per cent. in California.

These amounts may, however, in the author's opinion, be regarded as *minima*.

" It is questionable if the average plant as ordinarily conducted in California for some years past has been recovering 75 per cent. of the value in the ore " (*Bradley*).

According to Landers,* in all probability the losses in fine ore furnaces in America exceed 25 per cent., and may even reach as high as 40 per cent. on extremely low-grade ores and with too much air. Coarse-ore furnaces, on account of the small amount of draught necessary, do not incur so great a loss when proper attention is paid to the control of the air admitted into the furnace, and the smallest losses of all should be met in properly operated retorts or muffle furnaces. The losses sustained in treating low-grade ores in furnaces will in all probability be greater than that of wet concentration with a proper retorting of the concentrate.

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* Landers, *Eng. and Min. Journ.*, Oct. 1916.

No satisfactory economic process for the extraction of mercury, either by wet or by electrolytic methods, has yet come into favour.

A wet method for the recovery of mercury existing as sulphide in amalgamation tailing is, however, in operation at the Buffalo mines, Cobalt, Ontario.[*]

The mercury sulphide is dissolved out of the tailing with sodium sulphide in the presence of caustic soda, and the mercury from the double sulphide thus formed is precipitated by means of granular aluminium. The reactions are as follows :—

$$Na_2S + HgS = Na_2S, HgS.$$
$$3Na_2S, HgS + 8NaOH + 2Al = 3Hg + 6Na_2S + 2NaAlO_2 + 4H_2O.$$
$$2NaAlO_2 + Ca(OH)_2 = 2NaOH + Ca(AlO_2)_2.$$

It is claimed that this method should be equally applicable to cinnabar ores. With a clean cinnabar ore the mercury would be obtained wholly in the fluid form without retorting, and by straining through canvas it would be ready for market. Over 40,000 lbs. mercury has been recovered at the Buffalo mines by this process.

"The writer is of the opinion that either concentration or the alkaline sulphide solution method can be economically adopted at some quicksilver properties, depending on the nature of the ore and gangue associations; but it does not appear that they are likely to any considerable extent to displace the Scott furnace. Concentration may also serve as an adjunct to some existing furnace plants, to increase their capacity, as is at present being done at New Idria" (*Bradley*).[†]

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[*] E. B. Thornhill, *Min. and Sc. Press*, June, 1915.

[†] Bradley, *Quicksilver Resources of California*, p. 353.

ZINC AND CADMIUM.

ZINC.

Zinc is commercially known as *spelter.* Its existence was unknown to the ancients as a separate metal, although brass—that is, the copper-zinc alloy—was made by the Romans shortly before the Christian era, and used both for coins and ornaments. It was produced by heating together copper, calamine, and charcoal.

Physical Properties.—Zinc is a white metal with a bluish-grey tint. The fresh fracture of a cake of commercial zinc "spelter" presents large and very brilliant cleavage planes, especially when the metal is free from iron. The fracture is more largely crystalline the higher the temperature of casting is above the melting point of the metal. It is a comparatively soft metal, but is harder than tin. Variations in properties at rising temperatures indicate three allotropic varieties of the metal, α, stable up to about 170° C., β, stable between 170° and 330° C., and γ, stable between 330° and the melting point, 419° C.

Malleability and Ductility.—At ordinary temperatures zinc is brittle, but between 100° C. and 150° C. it is sufficiently malleable to admit of being rolled into thin sheets and drawn out into wire.

Tenacity.—According to Karmarsch, 2,809 lbs. per square inch, when cast, and between 18,703 lbs. and 22,188 lbs., when in sheets or wire.

Specific Gravity.—The specific gravity of cast zinc ranges from 6·9 to 7·2, according to the temperature at which it has been cast and the manner in which it has been cooled. By rolling its specific gravity is increased to about 7·25.

Action of Heat.—The melting point of zinc is 419·4° C. (Bureau of Standards, Washington). It can be readily distilled at a bright red heat. Its boiling point is about 940° C. (*Moissan*). It burns in the air at a temperature as low as 500° C. (*Ingalls*).

Electrical Conductivity.—The electrical conductivity of zinc is 25·6 to 29·9, according to the determinations of several observers, silver being taken as 100.

Atomic Weight.—Its atomic weight is 65·37.

Chemical Properties of Zinc.—Zinc is not affected by dry air at ordinary temperatures. In moist air a compact coating of basic zinc carbonate is formed, which impedes the oxidation of the underlying metal. When molten, zinc is readily oxidized and at its boiling point it burns, zinc oxide being produced.

Water has no action on it at ordinary temperatures if air be excluded. At a red heat the metal readily decomposes the vapour of water, and is converted into oxide.

Zinc is soluble in most acids, and also, but less rapidly so, in alkaline solutions, especially if in contact with iron or platinum.

The metal possesses the property of precipitating all malleable heavy metals except iron and nickel from their solutions, and is in extensive use for precipitating gold from cyanide solutions in the cyanide process.

Zinc Oxide, ZnO.—An amorphous powder, white when cold and yellow when hot.

It is infusible *per se*, and practically non-volatile (*Percy*). According to Doeltz it volatilizes at about 1,200° C., the volatilization being increased between 1,360° and 1,400° C.

It is insoluble in water, soluble in acids and in solutions of ammonium carbonate, also in solutions of potassium and sodium hydrates. When fused with sodium carbonate in proportions up to 20 per cent. of the oxide well-melted products result.

The oxide is very largely used as a white pigment (zinc white).

Zinc oxide is readily reduced by carbon and carbon monoxide at a strong red heat, between 1,125° and 1,150° C. (*Boudouard*), and by hydrogen at a lower temperature. Metallic zinc at similar temperatures reduces carbon dioxide to carbon monoxide, zinc oxide being formed.

When carbon is employed as the reducing agent, the oxide of zinc and solid carbonaceous matter need not be intimately mixed, but the carbonaceous matter must be in excess to prevent the formation of carbon dioxide.

The oxide is also reduced by iron at a high temperature, and the whole of the zinc is volatilized.

Zinc Silicates.—At a high temperature ZnO combines with SiO_2 to form silicates, of which there are several, but two only occur native—viz., the hydrous ($Zn_2SiO_4 + H_2O$) and the anhydrous (Zn_2SiO_4) silicates. Both are completely reduced to metal when heated with carbon.

Zinc Sulphate, $ZnSO_4$.—Zinc sulphate is present in variable quantities in roasted blende, in the form of a basic salt which has escaped decomposition When such blende is distilled the carbon in the charge converts this sulphate into ZnS. The neutral sulphate, $ZnSO_4$, is very soluble in water, but the basic sulphates are nearly insoluble.

Zinc Sulphide, ZnS.—Found native as zinc blende.

Blende is practically infusible, but is somewhat volatile at very high temperatures (*Percy*).

Zinc sulphide combines with most of the metallic sulphides, decreasing their fusibility. When roasted in a finely divided state at a moderate red heat zinc oxide and zinc sulphate are formed, sulphur dioxide being evolved. By increasing the temperature to a strong red heat towards the end of the roasting, the sulphate will be completely decomposed, and only zinc oxide will remain. Zinc sulphide is not reduced by carbon at the temperature obtained in zinc retorts. At a bright red heat it is completely reduced by iron. When heated with lime it is not decomposed unless carbon be present, and then only when the lime is in excess. Hence iron and lime act favourably in the distillation of zinc ores by decomposing any ZnS which may have escaped conversion into ZnO in the operation of roasting. The amount of iron in the charge, however, must be such that it will not form silicates which will have a destructive action on the retorts. It is, however, held by some metallurgists to be doubtful whether carbon, iron, or lime have much if any action on zinc sulphide under the conditions which prevail in the ordinary retorts in zinc distillation.

Commercial Zinc or Spelter.—Spelter always contains lead and iron, these being the chief impurities. Cadmium is frequently present in small amounts.

In still smaller quantities, usually little more than traces, As, Sb, S, and Cu are also found. Tin may also occur in remelted spelter.

In special brands of American high-grade spelter the lead does not exceed 0·02 and the iron 0·01 to 0·02 per cent. (*Ingalls*).* In good ordinary brands from 0·4 to 1·0 per cent. of lead and 0·03 to 0·05 per cent. of iron are usual. In four English brands of ordinary quality analysed by the author the lead ranged from 0·4 to 1·5 per cent., and the iron from 0·025 to 0·05 per cent. Electrolytic spelter, which is now largely used in the manufacture of brass for special purposes, is often very pure, the lead and iron in some samples being as low as 0·01 each.

The following analyses of brands of European virgin spelter, by J. S. G. Primrose,† may be taken as typical:—

Brand.	Lead. Per Cent.	Iron. Per Cent.	Cadmium. Per Cent.	Tin. Per Cent.
V.M.G. (Belgium), . . .	0·66	0·26	nil	0·03
Vieille Montagne (Belgium), . .	2·00	0·04	0·07	nil
Freiberg (Saxony), . . .	1·03	0·04	0·02	0·07
Lazyhutte (Upper Silesia), . .	1·12	0·02	0·017	nil
Lipine Electrolytic (Upper Silesia),	0·06	0·01	0·005	0·02

The term "virgin" spelter signifies the metal which is obtained direct at one operation from the ore.

The highest grades of spelter are also termed "fine zinc."

In America metal produced direct from ore is called "primary zinc."

As regards the grades of spelter, at the annual meeting of the American Society for Testing Materials, held at Atlantic City, June, 1916, the standard specifications in previous use were revised, and are now as given in the following table:—‡

Grade.	Pb.	Fe.	Cd.	Total not over.
A. High grade,§ . .	0·07	0·03	0·05	0·10
B. Intermediate,§ . .	0·20	0·03	0·50	0·50
C. Brass special,§ . .	0·60	0·03	0·50	1·00
D. Selected,§ . . .	0·80	0·04	0·75	1·25
E. Prime Western, . .	1·50	0·06	..	..

The figures represent the maximum percentage of impurities allowable. This classification corresponds substantially to the understanding among American zinc smelters.‖

A remarkably pure zinc, known as "spectroscopically pure," ¶ is made on a small scale for scientific investigations requiring metal of the highest purity. It is prepared by a series of fractional distillations of "chemically pure" zinc under vacuum until the product shows no impurity lines when examined spectroscopically. The metal contains less than 0·0001 per cent. impurity and exhibits unusual resistance to tarnishing and to the action of hydrochloric and sulphuric acids, but not to nitric acid. In dilute hydrochloric acid a piece of this pure metal lost 0·02 per cent. by weight in the same time that a similar piece of commercial zinc entirely dissolved. It possesses unusual softness and a low recrystallization temperature, which prevents strain hardening in cold working.

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* Ingalls, *The Metallurgy of Zinc and Cadmium*, p. 573.

† *Journ. of the Institute of Metals*, No. 2, 1909, vol. ii., p. 234.

‡ *Eng. and Min. Journ.*, July, 1916.

§ To be free from aluminium.

‖ *Eng. and Min. Journ.*, Jan. 6, 1912.

¶ H. M. Cyr, *Am. Electrochem. Soc., Trans.*, 1927, vol. lii., p. 349.

The effects of impurities on the metal are as follows :—

Lead.—In spelter intended for rolling a small percentage of lead is desirable, and up to 1·0 or even 1·25 per cent. it has no injurious effects on the malleability or ductility of the metal. When the spelter, however, has to be used for making brass which has to undergo severe mechanical treatment, as, for example, the manufacture of cartridge cases, it should contain as little as possible, not exceeding 0·07 per cent.

Iron.—The effects of iron are to increase the hardness and brittleness of zinc and reduce its malleability, but when the refining by liquation has been properly conducted there is insufficient present to affect these properties. When iron is present in excessive amounts the bright cleavage planes of the fresh fracture of a cake will show grey specks scattered over them.

For spelter intended for the manufacture of brass 0·05 per cent. of iron is often specified as the limit, but it is best lower for brass of high ductility and malleability.

Zinc may be completely freed from iron by redistillation, the use of iron tools and appliances being avoided.

Cadmium.—Cadmium is rarely present in injurious proportions. It is especially liable to occur in brass-special spelter when this is made as in America by collecting apart the first spelter which distils over, owing to the fact that cadmium is more volatile than zinc, and most zinc ores contain it. For the same reason it is frequently present in redistilled zinc.

In two plates of a sample ½-ton of so-called pure redistilled spelter the author found 5·08 per cent. of cadmium, but this is very exceptional. Muntz metal made with this spelter broke with a crystalline fracture closely resembling that produced by antimony.

"For some purposes cadmium in spelter, even a small percentage of it, is deleterious. In spelter that is to be used for slush castings there is no doubt about it. In spelter for brass-making there is not the same certainty. For brass that is to be cast and machined, the adverse effect of cadmium is probably overestimated, and it may not be adverse at all. For cartridge brass it is objectionable. In many cases where cadmium is objectionable it is not unlikely that there is hair-splitting about hundredths of a per cent. that is unnecessary" (*Ingalls**).

At present we have no trustworthy information as to the effects of small amounts of cadmium on brass or the other alloys of which zinc is a constituent.

However, no sensible effect on the physical properties of zinc is produced, even when 0·1 per cent. is present, and nearly always the percentage does not reach that amount. It is said to discolour "zinc white" made from zinciferous materials containing it.

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* *Trans. Inst. of Metals*, Sept. Meeting, 1916.

Arsenic, Antimony, Copper, Sulphur, and Carbon.—These elements are scarcely ever present in sufficient quantities in spelter to affect its properties either for rolling or the manufacture of alloys. Arsenic, however, should be absent in zinc intended for the precipitation of gold in the cyanide process, as in treating the precipitate with acid arseniuretted hydrogen is given off, and this has resulted in several fatal accidents.

Tin.—Tin tends to make zinc very hard and brittle in rolling, and although it is not of common occurrence, except in remelted spelter, yet it should always be looked for.

Aluminium.—In alloys, aluminium is frequently very injurious, 0·01 per cent. in many cases making brass useless for the purpose for which it is intended. In the few instances where its presence is desired, it is more satisfactory to add it directly than as a constituent of the spelter. The specifications (as proposed for the American Society for Testing Materials in 1916), therefore, require that the four higher grades of spelter shall be entirely free from aluminium.*

Industrial Uses of Spelter.—By far the greater proportion of spelter is used in the process of galvanizing iron and steel, over 60 per cent. of the total metal produced and imported into the United States being consumed for this purpose. A considerable but lower percentage is employed, about 18 per cent., in the manufacture of brass, and somewhat less in the manufacture of sheets.

As a constituent of alloys it is of the greatest importance and value, even in those in which it is not the principal metal, as, for example, the various kinds of brass (Cu-Zn alloys, (see p. 62). It is also frequently added in small quantities to the copper-tin alloys, the bronzes, especially statuary bronze, in order to ensure sound castings, and is a common component of the copper-nickel alloy, German silver, in which it is used to replace more or less of the more expensive metal nickel (see p. 65).

There are but few true zinc alloys—*i.e.*, those in which zinc is the chief constituent; the following, however, are in industrial use:—

	Zn.	Sn.	Cu.	Sb.	Pb.
Antifriction metal, .	85·0	. .	5·0	10·0	. .
Babbits' metal, so-called,	69·0	19·0	4·0	3·0	5·0

Zinc alloys readily with tin, and a useful metal for foundry patterns consists of zinc 75·0 and tin 25·0 per cent.

It also alloys with aluminium, silver, antimony, bismuth, and nickel, and forms amalgams with mercury. Of these, the Al-Zn alloys alone are of importance. They are largely used for light castings in the automobile industry (see pp. 603, 605, 606).

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* Stone, Bassett, and Price, *Report of the Committee on Non-Ferrous Metals and Alloys.* (*American Society for Testing Materials*), *Eng. and Min. Journ.*, August, 1916.

In several metallurgical operations zinc plays an important part, notably in the precipitation of gold in the cyanide process (see p. 325); the desilverization of argentiferous lead by the Parkes process (see p. 232); and the reduction of silver chloride in gold refining (see p. 359).

Zinc, in the form of slabs or anodes, is largely used for the prevention of corrosion in boilers.

Ores of Zinc.

The chief ores of zinc are blende and calamine. The oxide zincite is unimportant, although zinc is obtained from it in New Jersey.

Zinc Blende, Black Jack, ZnS.—When pure it contains 67·03 per cent. of zinc, but nearly always a considerable quantity of iron sulphide is present. It often contains cadmium, as much as 3·2 per cent. being found in some specimens, and is frequently associated with galena, iron pyrites, and copper pyrites. It sometimes contains sufficient silver for profitable extraction. As much as 95 ozs. per ton have been found. It is very widely distributed. In Great Britain, Spain, the Rhine districts of Germany, Westphalia, Sweden, Missouri, Kansas, and Colorado in the United States, the larger part of the ore produced is zinc blende. At the present time it is the chief source of zinc, and as received at works it usually contains 30 to 55 per cent. Zn.

Calamine, also sometimes called Smithsonite.—Zinc carbonate ($ZnCO_3$) contains 52·02 per cent. of zinc when pure. It was once the chief source of zinc, but the deposits in many localities are more or less exhausted, although in Upper Silesia, Austria, Italy, Greece, and Algeria the larger part of the ore produced is calamine.

Hemimorphite or Electric Calamine.—Hydrous zinc silicate ($Zn_2SiO_4+H_2O$). It is associated in New Jersey with Franklinite, but elsewhere generally with calamine. In Sardinia it occurs in considerable quantities.

Willemite, Zinc silicate (Zn_2SiO_4).—Occurs with calamine near Aix la Chapelle, and with Franklinite in New Jersey.

Both these ores are commercially termed calamine. Neither are important as sources of zinc, except Willemite in New Jersey, where it is separated by a magnetic process from Franklinite, and is treated for the production of the metal.

Franklinite.—An ore of iron, manganese, and zinc, in which the zinc varies considerably, but may reach 21 per cent.

It occurs in considerable quantities only in New Jersey, where it is treated for the production of zinc white and spiegeleisen (see p. 499).

Broken Hill Ore.—A complex sulphide, consisting of an extremely intimate mixture of zinc blende and galena, which occurs on a vast scale at Broken Hill (New South Wales). It is very variable in composition, the crude ore containing from 10 to 19 per cent. zinc, 15 to 25 per cent. lead. and about 20 ozs. of silver per ton, in a gangue of rhodonite, garnet, quartz, and calcite. The zinc mineral is not true zinc blende, but a variety, marmatite, in which the zinc is partly replaced by isomorphous iron and manganese. It is this mineral which causes so much of the trouble in roasting the Broken Hill concentrate, for while the oxides of iron and manganese probably exert a beneficial catalytic action in assisting the removal of the sulphur, they also tend to form a compound of zinc, manganese, and iron oxides practically free from silver and lead and similar in composition to the mineral franklinite which accumulates on the hearth of the furnace, and, if not removed, ultimately breaks the rabbles of the mechanical furnaces (*Moulden*).*

The ore is dressed to obtain a lead concentrate for smelting, and a zinc concentrate for spelter works ; the resulting slime which has accumulated in immense quantities it is hoped to smelt in electric furnaces (see p. 506).

A typical analysis of the zinc concentrate as delivered to the metallurgist is given by Mr. J. C. Moulden,† as follows :—

Zn,	46·50
Pb,	8·50
Fe,	7·60
Mn,	1·60
S,.	28·50
SiO_2,	4·50
Carry forward,	97·20
Brought forward,	97·20
Al_2O_3,	0·40
Cu,	0·18
O (organic matter and loss),	1·30
Cd,	trace
	99·98
15 ozs. Ag per ton.	

The chief countries for the production of zinc ores are—Germany, the United States, Australia, Italy, Spain, Algeria, Tunis, Greece, and Sweden.

Extraction of Zinc.—Zinc is largely extracted from its ores by the method of distillation. The oxide obtained by calcining the carbonate (calamine), or by roasting the sulphide (zinc blende), is the material almost exclusively employed in its manufacture, only a comparatively small quantity being obtained from the silicates (willemite and hemimorphite). It is mixed with coal, charcoal, or coke, and exposed to a very high temperature in fireclay retorts. The carbonaceous matter must be in excess to prevent the formation of CO_2, which acts as an oxidizing agent on the metal. The zinc distils off, is collected in clay condensers, and a continuous stream of CO issues from the retorts.

As has been already pointed out, zinc cannot be precipitated from its solutions by the common metals, and hence cannot be thus obtained in the metallic state. If other precipitants are used, and it is obtained as oxide, that oxide must be treated by a distillation process with carbon in order to obtain the zinc as metal.

There is hence no wet process by which metallic zinc can be obtained, although a wet process sometimes may be used to obtain a material rich in zinc for subsequent treatment by the distillation process.

Many methods have been suggested and experimented with for the electrolytic separation of zinc from its ores, but none, so far, has been sufficiently successful on a commercial scale to compete with the distillation process for ordinary spelter, although a large quantity of specially pure zinc is now being satisfactorily produced (see p. 503).

The extraction of zinc from its ores in the dry way—*i.e.*, by the distillation process—depends on the reduction of zinc oxide by carbon or carbon monoxide, so that ores consisting of zinc carbonate (calamine) must first be calcined, and zinc sulphide ore (zinc blende) must first be roasted, in order to convert their zinc into oxide. Zinc silicates are also reduced by carbon, but require a higher temperature than the oxide.

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* *Journ. Soc. Chem. Ind.*, 1919, p. 178 R.

† Moulden, *Journ. Royal Society of Arts*, 1916, p. 502.

Although the reduction of zinc oxide begins below the boiling point of the metal, yet it is only complete at above the boiling point so that the metal is separated in the form of vapour which has to be condensed. Air, vapour of water (steam), and carbon dioxide must not be allowed to come in contact with the gaseous zinc or it will be oxidized.

The condensation of the gaseous zinc to fluid zinc is a matter of some difficulty, as it can only be effected within a limited range of temperature—viz., between 415° and 550° C. Below 415° it condenses to a powder called zinc fume—*i.e.*, metallic zinc in the form of powder mixed more or less with ZnO (8 to 10 per cent.). If much above 550° it is not condensed at all. There is likewise another difficulty. If the zinc vapour is much diluted with other gases it will not condense to fluid zinc, but as *zinc fume.*

On account of the cost of the clay vessels in which the ore is treated, the loss of zinc due to the permeability of their walls, their liability to crack, and the consequent escape of zinc vapour, the amount of zinc absorbed by them and the large consumption of fuel, several attempts have been made to use shaft furnaces for the extraction of the metal, but without success so far as the production of metallic zinc is concerned.

In shaft furnaces the zinc can be reduced and separated from the ore as vapour, but the vaporized zinc is much diluted with carbon monoxide and nitrogen, and is besides more or less oxidized by the carbon dioxide invariably present, so that only zinc fume is produced. Moreover, zinc oxide can only be reduced by carbon monoxide when carbon dioxide is present in extremely small proportions, less than 0·8 per cent.

A process known as the Coley * process is being developed; a mixture of the ore and carbon is passed through a preheater into a revolving cylinder kept at the temperature necessary for reduction. The tube, made of cronite or some other suitable metal, is externally heated to 1,100° C., the internal temperature being about 1,050° C. It is claimed that a good extraction of the metal is obtained in the comparatively short time of 2½-3½ hours, the product being distilled to spelter.

Preliminary Preparation of the Ores.—Ordinary wet methods for the concentration of zinc ore have been largely superseded by the flotation process.

Flotation has necessitated finer crushing, but it has been found that higher recoveries are obtained while the grade of the concentrate is improved owing to more complete elimination of the gangue.

Calcination or Roasting.—The objects are :—

1. *In Calcining Calamine.*—To expel the carbon dioxide, and so convert the zinc carbonate and the calcium and other carbonates which may be associated with it into oxides. To expel water and render the ore porous.
2. *In Calcining Hemimorphite.*—To expel the water of hydration.
3. *In Roasting Zinc Blende.*—To convert the zinc sulphide into oxide, and the iron and other sulphides which may be present into oxides, and to

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* *Trans. Inst. Min. and Met.*, 1928, vol. xxxvii., p. 255.

volatilize and expel as far as possible any arsenic or antimony which may be present.

Calcination of Calamine.—Carbon will reduce zinc from zinc carbonate just as it does from zinc oxide, but, in the former case, the process of distillation would be delayed and the temperature lowered by the explusion of CO_2 and H_2O in the retorts, and besides the amount of these gases given off would dilute and oxidize more or less of the zinc vapour.

The greater the amount of calcium carbonate present the higher will be the temperature required for the expulsion of the CO_2. If the calamine be tolerably pure, a moderately red heat will suffice. The operation is frequently performed at the mine in order to save freight.

In Sardinia, where there are the most important deposits of calamine, the methods which are employed for the calcination of the ore are typical of the best practice in Europe, and may be summarized as follows :—

Unlike zinc blende, the ore need not be crushed fine, and the lump ores are calcined in simple shaft furnaces of circular section, about 6 feet 6 inches diameter at the bottom, and of somewhat smaller diameter at the top, to facilitate the descent of the charge. They range in height from 12 feet at some of the smaller mines to 18 feet 9 inches at Monteponi, and are of three types, viz. :—

(*a*) The older with a cone at the base between which and the sides the calcined ore is raked out.

(*b*) The latest type, with a grate of iron bars which admit of being turned for the discharge of the ore.

(*c*) A furnace fitted with two opposite fire-places, between which the ore passes out down two shoots.

In (*a*) and (*b*) the raw ore is charged in with alternate layers of coal ; in (*c*) the heat necessary for calcination is supplied by the external fire-places.

For mixed lump and fines a reverberatory furnace with inclined bed using gas as fuel is also employed at Monteponi, whilst for fine ore revolving cylindrical furnaces with continuous discharge are employed (see p. 40).

Roasting of Zinc Blende.—The process consists in heating the ore in a suitable furnace in an oxidizing atmosphere, when sulphur is oxidized to SO_2, and zinc oxide and zinc sulphate are produced. If the heat is then further increased, the SO_3 is driven off from the zinc sulphate and zinc oxide remains.

Of all the sulphides with which the metallurgist has to deal, sulphide of zinc is one of the most troublesome to roast sweet.

It may sometimes be advisable to roast the blende at a good centre for the distribution of sulphuric acid and re-ship the roasted ore to a satisfactory point for zinc distillation.

The blende must be reduced to a powder, the particles not exceeding 2 mm. in size.

In roasting blende, there may be two objects :—

(*a*) To prepare it for ordinary distillation.
(*b*) To prepare it for leaching.

In the case of (*a*) the procedure will be to roast the ore as dead as possible and avoid the retention of zinc sulphate in the roasted product. In the case of (*b*) to effect the roasting in such a manner that there shall be a maximum production of zinc sulphate and a minimum of insoluble zinc ferrite.

In both cases it is essential that the roof of the roasting furnace should be as low as possible, that the rabbling be vigorous, with as free an admission of air as can be arranged without unduly lowering the temperature.

(*a*) In roasting zinc blende to prepare it for distillation, the sulphur must be reduced to the lowest possible amount, both that existing as sulphides, and also as zinc sulphate, as the latter in the distillation process is converted into zinc sulphide by the coal or coke in the retort, and the zinc sulphide formed is not reduced, but is left in the residue. Not more than 1 per cent. of sulphur should be left in the roasted ore, but frequently more is present. This is owing to the formation of $ZnSO_4$ during the roasting from the conversion of part of the SO_2 into SO_3 by the hot ore and hot walls of the furnace and the oxidizing furnace gases. This SO_3 combines with the ZnO, forming $ZnSO_4$.

The changes which occur in the ZnS during the operation may be represented by the following equations :—

$$ZnS + 3O = ZnO + SO_2.$$
$$2ZnS + 7O = ZnO + ZnSO_4 + SO_2.$$

At a higher temperature

$$ZnSO_4 = ZnO + SO_3.$$

Galena is converted into lead oxide and sulphate, or if the blende contains much quartz, into lead silicate. Iron and copper sulphides are oxidized as in pyritic roasting.

If the temperature of calcination is low, also if other sulphides are present, the larger is the proportion of $ZnSO_4$ formed. If a very high temperature is reached many difficulties arise, especially when the blende is impure. Thus, in the presence of quartz with iron or lead, silicates may be formed, and these will fuse and envelop particles of the ore, and prevent their oxidation. Lead sulphate will also fuse and act similarly. Quartz alone has no effect.

Calcspar on roasting with blende is partly converted into oxide and partly into sulphate, according to Prost, calcium sulphate exerts no retarding influence on the reduction of zinc oxide.

Barytes is unchanged. In the distillation retorts it is converted by carbon into BaS, which probably is as harmless as calcium sulphate (*Ingalls*).

Fluorspar must be removed from blende intended for use in the manufacture of sulphuric acid ; as the investigations made by Truchot show that lead is attacked by sulphuric acid containing small quantities of hydrofluoric acid, hence the life of the sulphuric acid chambers and of the Glover's towers will be shortened if the blende contains this mineral.

The loss of zinc in roasting by dusting and volatilization is generally about 2 per cent., and if the blende is argentiferous the loss of silver may reach 10 per cent.

In order to effect a satisfactory roasting of blende for distillation the procedure should be as follows :—The blende should be deprived of most of its sulphur before it reaches the hottest part of the furnace, and when there, according to Hommel,* "it must be brought into contact at a temperature not much exceeding 800° C., with lively stirring and a heavy current of air without being chilled. As zinc sulphate, according to Landis, decomposes completely and quickly in a current of air at 760° C., a higher temperature than 800° C. is unnecessary."

In muffle roasters worked with a finishing temperature not exceeding 950° C. on Broken Hill concentrate of the composition given on p. 464, the roasted product may contain as little as 1 per cent. sulphur. The temperature in roasting the ore must, in fact, not be excessive, otherwise losses of metal by volatilization, particularly silver and lead, attain serious proportions (*Moulden* †).

To obtain the most satisfactory roasting of blende for distillation, "the roasting furnace must be so constructed that it will fulfil the following conditions:—(1) The ore must be quickly brought to the temperature of ignition, which is produced by external heat or by the hot roast gases; (2) the ignited blende must be deprived of most of its sulphur by vigorous rabbling and moderate draught, but without external heat; (3) the almost desulphurized blende must be brought in contact, at a temperature not exceeding 800° C. and lively stirring, with a heavy current of air without getting chilled; (4) the height of the roof of the hearth must be as low as possible, in order to obtain the maximum oxidizing power of the air" (*Hommel* ‡).

As regards the production of zinc ferrite in dead roasting, Hommel found in roasting a Tasmanian ore containing 18 per cent. of iron, that, after the largest proportion of the sulphur had been removed at the lowest possible temperature, the ore could be exposed to the highest heat obtainable in a roasting furnace without any ferrite being formed.

(*b*) In roasting blende for leaching, especially if it is very ferruginous, the operation should be conducted at the lowest possible temperature, the maximum amount of zinc sulphate will then be produced, and but little or no zinc ferrite as a temperature exceeding 1,000° C. is required for the formation of this insoluble substance.

It is quite possible to obtain 60 or even 70 per cent. of the zinc in a blende as sulphate, especially if the latter contains iron, only the furnace temperature in roasting must not exceed 600° C. In order to attain this end, the external heat must be restricted as much as possible, the muffle should even be cooled down if it is desired to accelerate the process by an increased draught and livelier rabblings (*Hommel* §).

From what has just been stated regarding the roasting of zinc blende, it is evident that it cannot be roasted like calamine in shaft furnaces, and, therefore, that either reverberatory furnaces or muffle furnaces must be used. Sometimes, however, when the sulphur of the blende has not to be utilized in the manufacture of sulphuric acid, a preliminary calcination in stalls, or shaft furnaces, is carried out to remove the excess of sulphur, and to break up the ore, the products being afterwards ground and calcined in reverberatory furnaces or muffles. If it is desired to utilize part of the sulphur for the manufacture of sulphuric acid, burners may be used, and, of course, in such cases reverberatory calcination must follow, as the residue will contain about 8 per cent. of sulphur.

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* *Eng. and Min. Journ.*, Oct. 1912. Trans. from *Metallurgie*, May, 1912.

† *Journ. Royal Society of Arts*, 1916, p. 508.

‡ *Loc. cit.*

§ *Loc. cit.*

The furnaces employed for roasting the ground zinc blende are of many kinds, the more important being the following :—

Reverberatory furnaces—

1. Hand-raked, with one hearth.
   ,, ,, two superimposed hearths.
   ,, ,, shelf burners.
2. Raked mechanically—Brown horse-shoe furnace.
   ,, Ropp straight-line furnace.
   ,, Zellweger furnace.
   ,, Merton furnace.
3. Muffle furnaces in use for burning blende for sulphuric acid manufacture—
   Hegeler furnace.
   Hasenclever or Rhenania furnace.
   Spirlet furnace.
   Delplace furnace.

According to Ingalls,* practice has settled down upon the Hegeler, Merton, Ridge, and Spirlet as the standard mechanical muffle furnaces, but among these only the Hegeler finds general application, although it appears to be passing out of use. In places where hand-raked furnaces are still permissible by virtue of labour conditions the Delplace would probably be adopted in preference to any other.

Reverberatory Furnaces in which the charge is raked by hand.

These are gradually being replaced by the more economical and effective mechanically rabbled and muffle furnaces, although there are many still in use. They are built either with single or with two superimposed hearths, but the former is only in very limited use, the latter being used in Europe. The length of the hearth in roasting sulphides is determined by the percentage of sulphur in the ore. Hence with ordinary blende containing 20 to 25 per cent. of sulphur, where the hearth is single, the length is usually 40 feet, but where there are two hearths one above the other the total length is 48 feet.

In the general features of their construction they resemble the roasting furnace (Figs. 2 and 3, p. 24), but they differ from it in having narrow hearths about 8 feet wide, and the working doors are only on one side, two furnaces being commonly built back to back. Each double-hearth furnace of the above dimensions will roast about 2 to 3 tons of ore per twenty-four hours down to about 1 to 1·5 per cent. of sulphur.

Shelf Burners.—This type of furnace (Figs. 182 and 183),† was largely used for blende roasting in Kansas and Missouri, although mechanical furnaces have recently displaced it almost entirely. There are, in fact, at present not more than two or three hand-worked furnaces in America. They are simple reverberatories, each having usually four superimposed small hearths about 8 feet long by 8 feet wide. The working doors are at one end, and the ore is drawn towards the working door on one hearth, and pushed away from it on the next one below. The ore is thus raked from shelf to shelf, and is discharged through an opening in the bottom shelf into a vault below.

They are usually built in blocks of four. A four-hearth burner of the above dimensions will roast about 5 tons of raw ore in twenty-four hours, reducing the sulphur to about 1 per cent. Both coal and gas are in use as fuel.

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* W. R. Ingalls, *Eng. and Min. Journ.*, Jan. 1919, p. 87.

† Ingalls, *Metallurgy of Zinc and Cadmium*, pp. 80, 81.

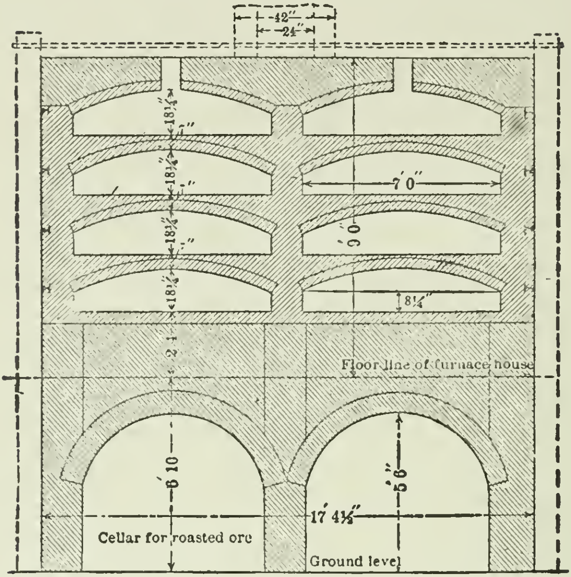
42"
24"
18¼"
18¼"
18¼"
18¼"
7' 0"
9' 0"
8¼"
2' 1"
Floor line of furnace house
6' 10"
5' 6"
17' 4½"
Cellar for roasted ore
Ground level

Fig. 182.—Shelf Kiln used in Texas. Transverse Section.

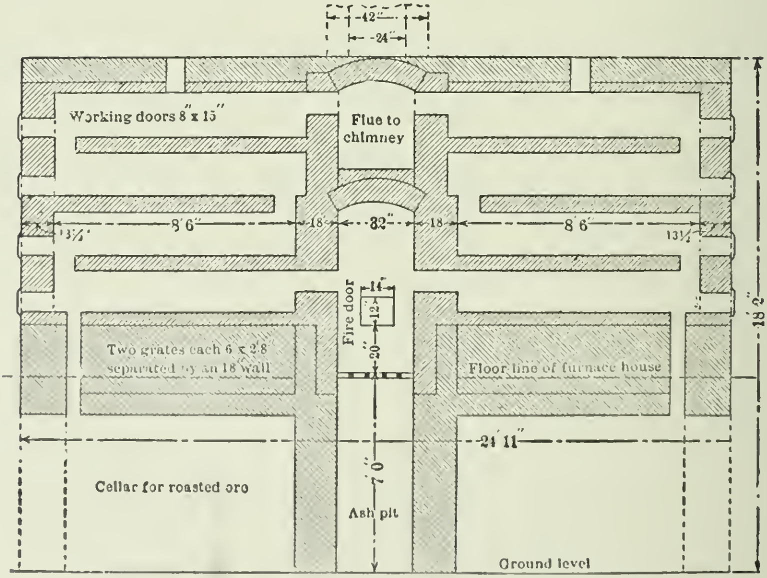
42"
24"
Working doors 8" x 15"
Flue to chimney
13½"
8' 6"
18
32"
18
8' 6"
13½"
Fire door
14"
12"
20"
Two grates each 6' x 2' 8" separated by an 18" wall
Floor line of furnace house
24' 11"
18' 2"
7' 0"
Cellar for roasted ore
Ash pit
Ground level

Fig. 183.—Shelf Kiln used in Kansas. Longitudinal Section

Reverberatory Furnaces worked Mechanically.—Owing to the higher temperature required for the decomposition of the zinc sulphate at the end of the roasting, the wear of the rakes and iron parts is much greater than where ordinary pyrites is roasted.

The Brown Furnace.—According to Ingalls, only the old " horse-shoe " form of this furnace has been used in the United States for blende roasting, but the later " straight-line " furnace (see Fig. 4, p. 26) is much superior.

The capacity of a Brown " horse-shoe " furnace with a hearth 135 feet long and 8 feet wide is about 11 to 12 tons of raw ore roasted down to 1 per cent. or less sulphur in twenty-four hours.

The Ropp Straight-Line Furnace (see Fig. 8, p. 28).—A large number of these furnaces were in use at the works of the Lanyon Zinc Company, but they have lately been modified by supporting the hearth on standards to allow air to circulate beneath it, with arrangements for admitting air through the slit in the hearth and controlling its amount. A Ropp furnace, 150 feet by 14 feet, will roast 18 to 21 tons of raw blende down to 0·9 per cent. sulphur in twenty-four hours.

The Zellweger Furnace.—This furnace is now well established for blende roasting in Kansas and Oklahama, where the SO_2 in the gases is not utilized, although its consumption of fuel is large. It is a long hearth reverberatory furnace like the Brown " straight line," from which it differs in the form of the rabbles and the supporting mechanism.* At the Cherokee Lanyon Works a furnace, 135 feet by 15 feet, heated by natural gas roasts 18 tons of ore containing 30 per cent. sulphur down to 1 per cent. in twenty-four hours.

The Merton Furnace (see Fig. 12, p. 32).—In the Merton furnace the ore is stirred during its course at a livelier rate than in any other furnace, and this, together with the admission of hot air in the lowest hearth, ensures a perfectly dead roast. In Hommel's opinion, " this system fulfils the conditions of good blende roasting best of all. The only thing that can be said against the furnace is that at various places not reached by the rabbles dead corners will form, in which the ore remains untouched. In order to remedy this the idle ore may be pushed back into the circuit once a day by the attendant." †

This type of furnace is in successful use at two of the chief spelter works in Swansea. They are of the usual form, except that the finishing hearth and fire-place are of exceptionally large dimensions.

Muffle Furnaces.—In these furnaces the roasting is conducted in muffles, to which the furnace gases have no access, and the SO_2 is suitable for the manufacture of sulphuric acid.

In roasting zinc blende for the manufacture of the acid, the roaster gases should contain not less than 5 per cent. by volume of SO_2 for the satisfactory working of the sulphuric acid chamber. Here it may be mentioned that the contact system of sulphuric acid manufacture has been introduced with success in connection with the roasting of blende.

Hegeler Furnace (Figs. 184 and 185).—This furnace is employed in America in practically all the spelter works where the SO_2 from the roaster gases is utilized for the manufacture of sulphuric acid. It is also in use in one or two works where the SO_2 is not utilized.

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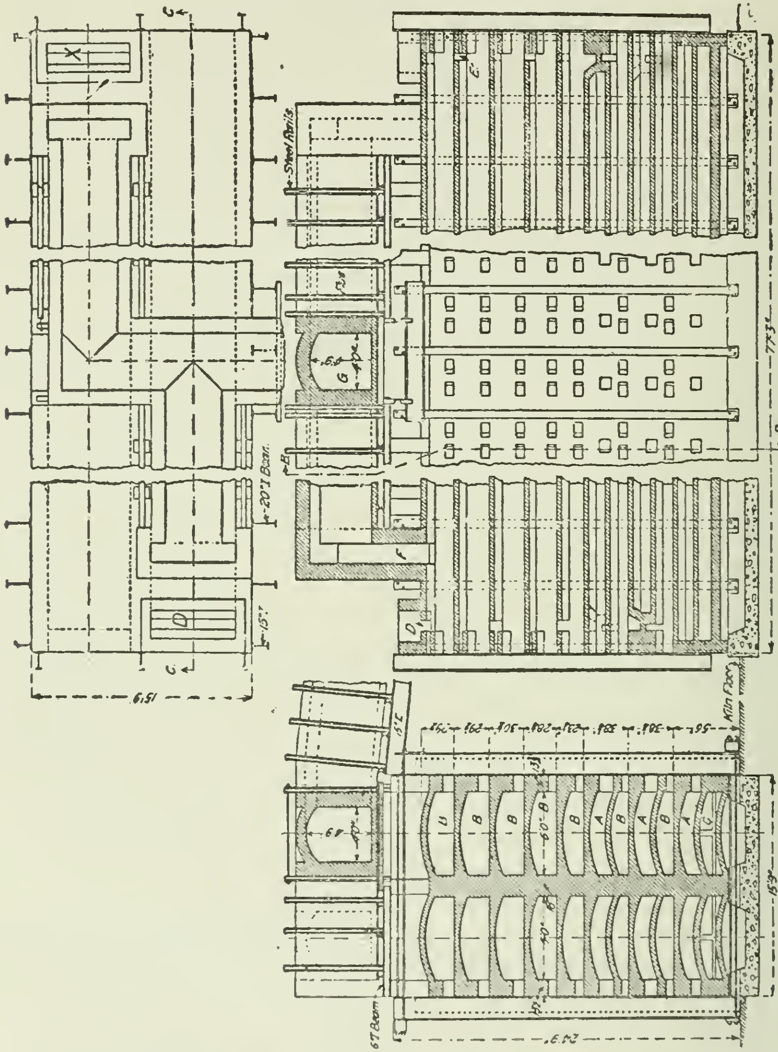
* For a full description, see Ingalls, *op. cit.*, pp. 112-115.

† *Eng. and Min. Journ.*, Oct. 1912.

The Hegeler furnace is a multiple-muffle furnace in which seven muffles are placed one above the other, two furnaces being built together to form one block. The three lowest muffles are heated by producer gas, the flame passing first under and then over them.


Section-C-G
Part Side Elevation
Section-C-C
Section-B-B
Steel Rails
20" I Beam
Kiln Floor
6" I Beam
X
D
G
E
F
A
B
C

Figs. 184 and 185.—Hegeler Furnace.

The muffles are usually 5 feet in width and from 70 to 80 feet in length. The ore is fed at opposite ends of the two top hearths, and is rabbled mechanically by rakes, so that it travels from hearth to hearth, and is finally discharged at the two opposite ends of the bottom hearths. Rabbling is commenced at the top hearth, the charge being moved towards the discharge end, where it is dropped through a slot in the floor of the hearth upon the hearth below. It is then drawn by another rabble toward the opposite end, where it is similarly dropped on the next hearth. The ore is thus moved from hearth to hearth until it is finally discharged. The rabbles are of the ordinary rake type (so designed as to ensure that the ore will be ploughed up from the bottom of the hearth whilst it is being moved forward), and are drawn through the furnace by detachable rods. The rods are supported on a frame at the end of the furnace. The frame has a series of supports corresponding to each muffle, and a series of rods resting on three supports in such a position that they can be thrust or drawn through the muffles. The frame also carries the mechanism for thrusting the rods in and drawing them out. The ore is rabbled every 1½ to 2 hours.

The furnace is fired with producer gas.

The gas travels in the opposite direction to the ore, being admitted to the lowest fire-muffle at one end, it passes to the other, and is partly burned by the admission of air at intervals. The gas then passes outside the muffle and is admitted through a by-pass to the next muffle above, where it is further burned, the combustion being finally completed under the third muffle. The hearths are closed at the ends by sheet-iron doors, which are hinged at the top and automatically opened and closed by the passage of the rabbles through the furnace.

The rakes and rods are longer out of the muffles than in them, so that the wear is said to be less than is the case in the working parts of other mechanically worked furnaces. A 75-foot furnace roasts about 40 to 50 tons per twenty-four hours, according to the quality of the blende, with a consumption of coal of about 20 to 25 per cent. of the weight of the raw ore. The gases from the roasting contain on an average 4·0 to 5·0 per cent. by volume of SO_2, and are utilized for the manufacture of sulphuric acid.

The Hegeler furnace has several disadvantages, the chief of which are :—The number of workmen required is high for a mechanically worked furnace. There is a large consumption of fuel and a comparatively low percentage of SO_2 in the gases. The intermittent rabbling if the ore tends to sinter.

On the other hand, it can be worked by any workmen under the direction of only a few skilled men.

Hasenclever Furnace (see Figs. 21, 22 and 23, pp. 42 and 43).—The most generally used muffle furnace in Europe, where it is usually worked by hand.

The most recent furnaces have four muffles, one above the other, each being 40 feet 9 inches long, divided by a middle portion into two divisions, each of which is 20 feet 3 inches long.

With ores rich in sulphur the two lowest muffles are heated externally, the two upper only receiving the heat resulting from the oxidation of the sulphides.

Capacity, 5 tons of blende roasted down to 1 per cent. sulphur in twenty-four hours, the roast gases containing 5 to 7 per cent. by volume of SO_2. Consumption of coal, about 25 per cent. of the raw ore.

The furnaces in common use in the United States for roasting blende are the Hegeler and the Zellweger, the former being employed invariably when the roast gas is used for sulphuric acid manufacture. In Europe, however, the roasting is still sometimes done in hand-worked roasters.

*The Spirlet Furnace** (Fig. 186).—" The furnace consists of three circular hearths which revolve around a central axis, which is, however, purely geometric, there being no interior working parts ; a fourth and lowest hearth is stationary, as is also the roof of the fire-box.

" The furnace structure is built up within six vertical columns, to which are fastened annular rails for supporting the movable hearths. These hearths are constructed within an engirdling spur gear, and are supported on wheels which run on annular rails, carried by the exterior framework. The spur gears mesh with small pinions attached to vertical shafts, which are connected with the source of power and constitute the driving mechanism, turning the alternate hearths in opposite directions.

" The hearths are slightly arched. They are constructed of special refractory tiling. On the under side the stirring rabbles, made of the same refractory material as the hearth itself, are dovetailed in. These rabbles are so arranged that with the rotation of the hearth the ore is moved, on one hearth outwardly from the centre, and on the next hearth inwardly towards the centre. Each hearth thus bears on its upper side the ore to be roasted, while on its under side are the rabbles which stir the ore upon the next hearth below.

" At the periphery, the roasting compartments are hermetically sealed by annular rings, which dip into the channel of the ring next below, made tight with a seal of sand or fine ore. The lowest hearth, which is stationary, is muffled, and is heated from a fire-box. There are arrangements for preheating the air which enters the roasting chambers.

" The advantages claimed for this furnace are that there are no working parts of iron within the furnace itself, and by virtue of their absence it is possible to make the distance between the several hearths very small, this being economical from thermal considerations. By avoiding iron stirrers, the cooling of any iron part is unnecessary, wherefore no heat is carried away from the furnace by cooling air or water. The cost of repairs is small, being confined substantially to the maintenance of the arches. The first furnace was in operation more than a year without any one of the stirring rabbles becoming broken. The several hearths can be easily removed, one after another, by simply lifting them out by means of a movable crane, it being unnecessary to detach a single screw or bolt. It is claimed that there is very little fine dust produced in roasting in this furnace owing to the drop from one hearth to another being so small.

" The average capacity of the Spirlet furnace is about 5 tons per twenty-four hours, with a power consumption of less than 2 horse-power. The labour attention is probably similar to what is required with furnaces of the MacDougall type. It is claimed that the fuel consumption is less than 10 per cent. of the quantity of ore charged. The sulphurous gas is strong, being 5 to 7 per cent. SO_2 by volume."

Compared with the Hegeler furnace, the number of workmen and the motive power required are much less, as also is the amount of dust produced, whilst the gas is richer in SO_2. As regards fuel, it has a lower consumption than that of any other blende-roasting furnace. A very highly refractory material is, however, necessary for its construction.

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* *Eng. and Min. Journ.*, Oct. 1914.

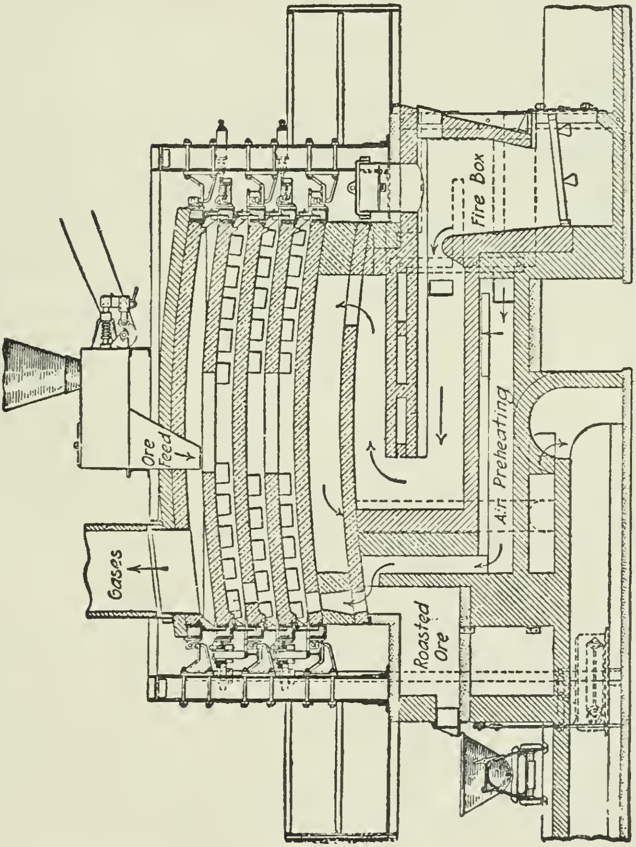
Gases
Ore Feed
Roasted Ore
Air Preheating
Fire Box

Fig. 186.—Spirlet Furnace.

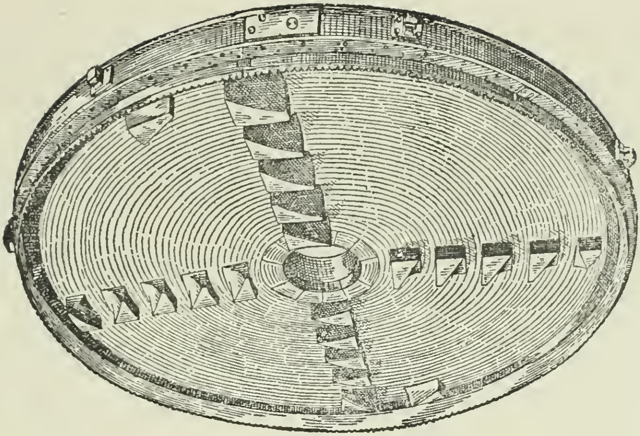

Fig. 186a.—View of one of the Hearths of Furnace.

Three Spirlet furnaces have been erected at the Rose Lake Works, Illinois, of the Granby Mining and Smelting Company. Others have been installed in some of the works of the National Zinc Company, U.S.

The Delplace Furnace (Fig. 187[*]).—This furnace is the most efficient of all the hand-worked furnaces in that it yields a gas rich in SO_2 and its consumption of fuel is very small. It requires, however, much skilled labour, and can hence be employed economically only in localities where fuel is dear if skilled workmen can be obtained at low wages.

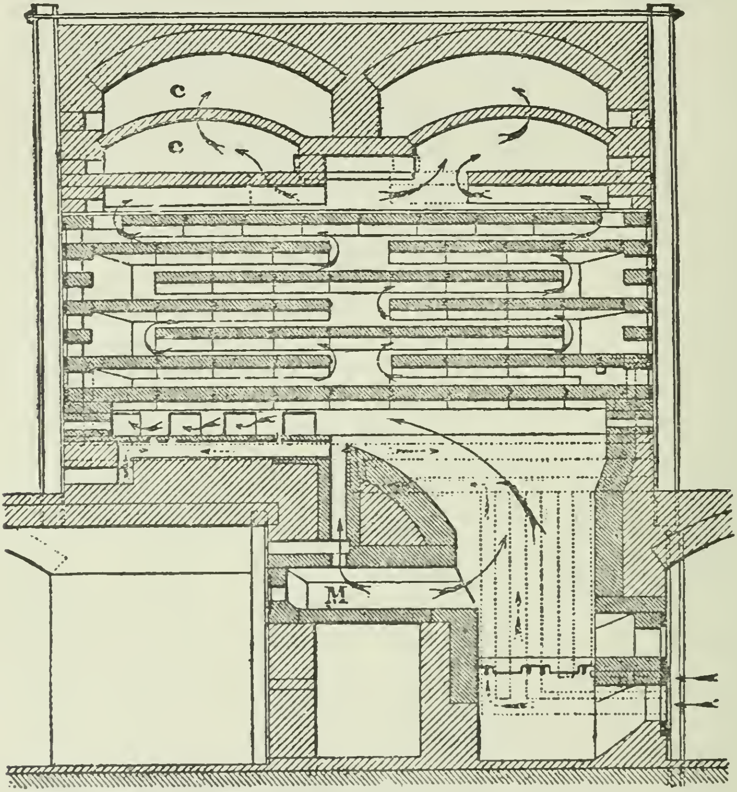

Fig. 187.—Delplace Furnace.

It has seven hearths, arranged one above the other, but each alternate hearth is divided into two parts by an opening about 1 foot 4 inches wide at the middle of the furnace.

When the ore is rabbled on one of these hearths it falls through this opening upon the middle of the hearth below it, which is not so divided. On this hearth it is drawn to each end, where it falls through an opening upon the divided shelf beneath it. The ore thus travels forwards and backwards until it reaches the lowest hearth and is discharged.

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[*] Prost, *Cours de Metallurgie des Métaux autres que le Fer.*, p. 43.

The gas after passing through the dust chambers above the hearths is led to the sulphuric acid plant.

The furnace is usually built in blocks of 6, 9, 12, or 18 units. Each group of 3 units is furnished with two fire-boxes built under the lowest hearth. Each fire-box is connected with a muffle, which is heated by waste heat and that radiated from the fire-box, and into which the coal is charged. In this muffle the coal gives up its volatile matter, forming coke. When the volatile matter is no longer given off, the coke is pushed into the fire-box, where it burns.

A recuperative system is also similarly built in, and by its means and an arrangement of flues, the air for the combustion of the fuel gases and for the oxidation of the sulphur in the blende is previously heated.

The height of the roasting space of each hearth is very low, about 6½ inches, and the doors through which the rabbling takes place are very small, only sufficiently large to admit a rake used in rabbling, hence but little heat is lost and the oxidizing action of the air well maintained. The gases from the roasting are said to contain on an average 6½ to 7 per cent. SO_2, a higher percentage than that obtained in any blende roasting furnace except perhaps the Spirlet and Ridge furnaces, and the blende is roasted to the utmost possible limit.

The consumption of fuel is only 10 per cent., and the quantity of dust produced is small.

A block of six furnaces is about 37 feet long and 23 feet broad.

From 2,300 lbs. to 4,000 lbs. of blende, according to its quality, is roasted in each furnace in twenty-four hours.

A great and serious drawback is that of labour.

In modern works in Belgium and Germany, Delplace furnaces have supplanted those of the Hasenclever type. They are also in use in France.

The Ridge Roasting Furnace[*] (Fig. 187*a*).—This furnace has been introduced in South Wales and elsewhere for roasting zinc concentrates and other purposes. The furnace has five hearths, one for drying and heating the ore, three for roasting, and one for cooling the ore and preheating the air. The ore is moved from hearth to hearth by rabbles hung on arms fastened to hollow, water-cooled shafts. Each of the four shafts is made in one piece, and the arms are fixed to the shaft in such a way that they can be renewed easily when necessary. The driving gear is placed on a solid foundation away from the heat, and is protected from the dust. The main driving wheels are independent of the shaft, which can be raised or lowered at will. The furnace is gas-fired, and the gas is burnt only under the bottom roasting hearth. The roasted product, when Broken Hill concentrates were used, reached a tenor of total sulphur as low as 0·75 per cent. on a 10 per cent. consumption of coal in the producers. The SO_2 content in the sulphur gases averages 6½ to 8¼ per cent. About 10 H.P. is required to operate one of these furnaces. One furnace treats 12 to 14 long tons per day. The fire gases leave the furnace at a high temperature and pass through a recuperator to preheat part of the air going to the furnace, while the rest of the air is preheated by the hot ore on the cooling hearth.

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[*] *Min. Mag.*, April, 1917. Abstract of paper by H. M. Ridge, *Eng. and Min. Journ.* Feb. 1917. M. F. Chase, *Eng. and Min. Journ.*, Oct. 1917.

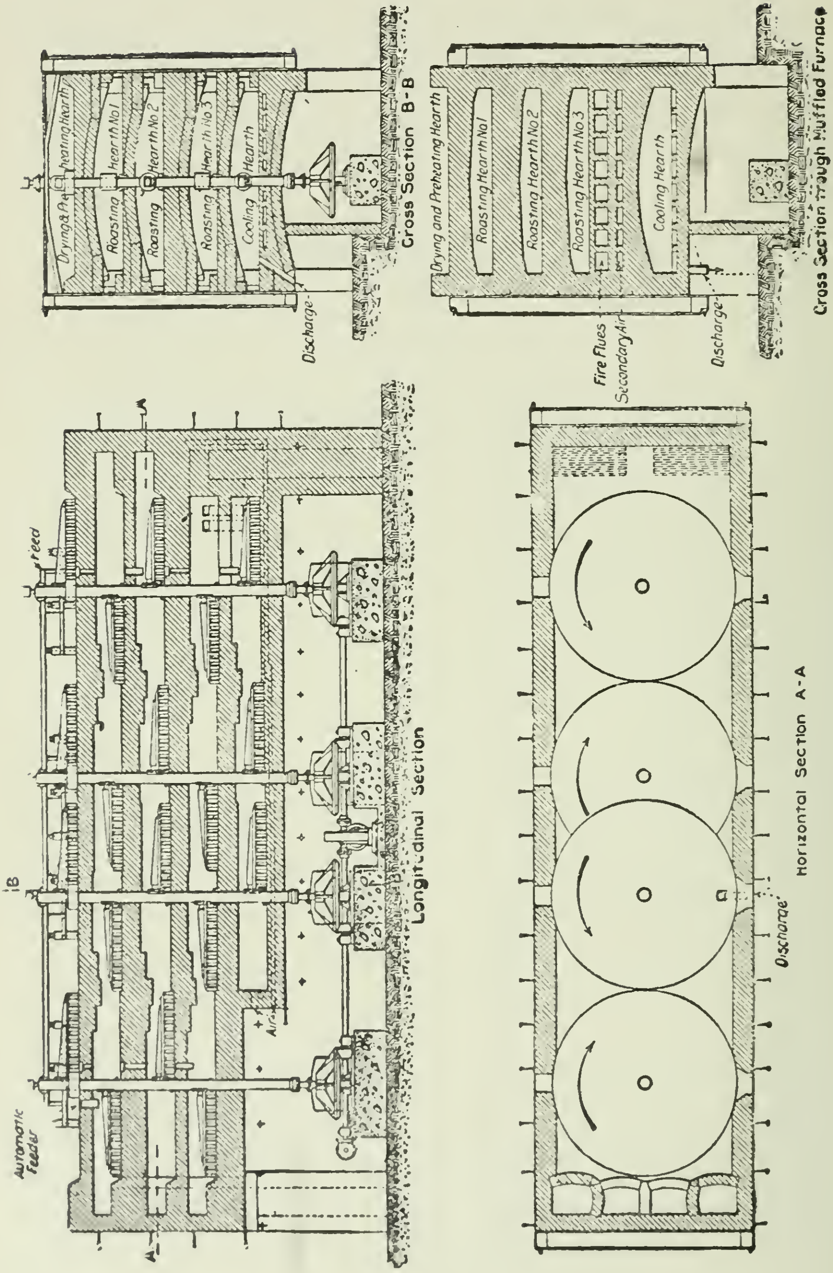
Drying & Preheating Hearth
Roasting Hearth No 1
Roasting Hearth No 2
Roasting Hearth No 3
Cooling Hearth
Cross Section B-B
Discharge
Drying and Preheating Hearth
Roasting Hearth No1
Roasting Hearth No 2
Roasting Hearth No 3
Cooling Hearth
Fire Flues
Secondary Air
Discharge
Cross Section Through Muffled Furnace
Automatic Feeder
Feed
B
A
Air
Longitudinal Section
Horizontal Section A-A
Discharge

Fig. 187*a*.—Ridge Roasting Furnace.

Roasting in Dwight-Lloyd Machines.[*]—The Dwight-Lloyd sintering process has been applied with promising results for the desulphurization and sintering of zinc sulphide concentrates at the Port Pirie smelting works of the Broken Hill Associated Smelters' Proprietary, South Australia. It has been found practicable to reduce partly roasted flotation concentrates from 26 per cent. sulphur down to 1 per cent. A portion of the gas, but not all, may be used for sulphuric acid manufacture.

The process is as follows:—The concentrates are at present pre-roasted in a Ropp furnace, fired with producer gas, down to 8 or 10 per cent. S. In order, however, to economize fuel, a Herreshoff has been installed for this purpose. The final roasting and sintering is carried out on a Dwight-Lloyd machine. The whole operation cannot be carried out on the D.-L. machine alone, as it was not found possible to keep the temperature of a bed of green ore on this machine below its melting point. The charge slagged badly, and needed repeated crushing and repassing over the machine.

A small amount of green ore is mixed with the pre-roasted concentrate to serve as an igniter, the amount added being equal to 2 per cent. of sulphur on the weight of pre-roasted material sent to the machine.

The roasted product leaves the D.-L. machine as a friable sinter which is easily crushed and works well in the retorts when crushed to pass through a $\frac{3}{8}$-inch ring. "Moreover, the sintered product gives astonishingly improved results in distillation, it having been found possible at Port Pirie to charge the retorts with 16·6 per cent. more ore with the use of 10 per cent. less of reduction material, while recovery of zinc increased 4·3 per cent., and there was slightly less loss of retorts. These figures were obtained by four months of operation with roasted and sintered blende, 50 tons per day being used, compared with the previous record of six months, when the furnaces were distilling ore roasted in Hegeler kilns."[†] A similar method of roasting is used in South Wales.

The Extraction of Zinc from the Calcined or Roasted Ores.—The process consists in heating the calcined or roasted ore with carbon in fire-clay vessels to a bright red or approaching a white heat, when the zinc is volatilized, and is condensed in fire-clay receivers or adapters, a stream of CO passing out of the retorts continuously during the operation.

The oxide obtained by roasting zinc blende requires a higher temperature for reduction than that from the calcination of the carbonate. Also, the higher the temperature at which zinc blende has been roasted, the higher is the temperature required for the reduction of the resulting oxide.

The reactions which may occur in the process are as follows, and are all endothermic:—

$$\begin{array}{llll}
(a) & \mathrm{ZnO} + \mathrm{C} & = & \mathrm{Zn} + \mathrm{CO} \\
 & -\ 86{,}000 & & +\ 29{,}000 = -\ 57{,}000. \\
(b) & 2\mathrm{ZnO} + \mathrm{C} & = & 2\mathrm{Zn} + \mathrm{CO}_2 \\
 & -172{,}000 & & +\ 97{,}000 = -\ 75{,}000. \\
(c) & \mathrm{CO}_2 + \mathrm{C} & = & 2\mathrm{CO} \\
 & -\ 97{,}000 & & +\ 58{,}000 = -\ 39{,}000. \\
(d) & \mathrm{ZnO} + \mathrm{CO} & = & \mathrm{Zn} + \mathrm{CO}_2 \\
 & -\ 86{,}000 - 29{,}000 & & +\ 97{,}000 = -\ 18{,}000.
\end{array}$$

Hence the application of external heat is necessary.

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[*] Gilbert Rigg, *Min. Mag*, June, 1918.

[†] W. R. Ingalls, *Mineral Industry*, 1919, p. 771.

The precise part played by CO in the reduction is doubtful, although CO certainly reduces ZnO. As has already been pointed out, the carbon must be in excess, as CO_2 oxidizes zinc vapour.

Any ferric oxide present will be partly reduced to metallic iron, and this will react with zinc sulphide, setting free zinc, but some will also form fusible ferrous silicates, which may not only coat the particles of ore and prevent their reduction, but will attack the sides of the retorts and perforate them, When lead is present in the ore part will be found in the residue and part will be volatilized and enter into the condensed zinc.

Gold and nearly all the silver remain in the residue, as spelter rarely contains either of these metals. Cadmium is volatilized and condenses with the first portion of the zinc.

There are three methods in use for the extraction of zinc from the roasted ores, viz. :—

1. *The Belgian.*—In which the furnaces have four to seven rows of retorts of circular section, but these are gradually being displaced by elliptical retorts.

2. *The Silesian.*—In which the retorts are large and muffle-shaped, and were formerly arranged only in one row.

3. *The Rhenish or Belgo-Silesian.*—In which the retorts are arranged in two or three rows, are always muffle-shaped or elliptical, and larger than the usual Belgian, but much smaller than the typical Silesian.

The Rhenish type of furnace is gradually replacing the Belgian and Silesian furnace on the Continent and England, but in the United States the Belgian furnace is still in very extensive use. There were formerly two other methods, the English and the Carinthian, but they are now obsolete, and only of historical interest.

Zinc Smelting in Vertical Retorts.—Attention may be drawn here to a *precis* by Mr. Walker in the *Mining Magazine,* July, 1916, of an article by M. Liebig in *Metal und Erz,* containing an account of a furnace with vertical retorts which is at work at Hamborn, Westphalia. It is said to be in successful operation, a continuous smelting of the ore being effected, all the old difficulties having been overcome. M. Liebig, however, gives no drawing of the furnace, and those contained in the British Patent specifications which are given in the *precis* do not tally with his description of the furnaces at Hamborn.

Retorts and Muffles (Figs. 188, 189).—The retorts employed in the Belgian method were formerly cylindrical, but now are more generally elliptical in cross-section. Their average length is 4 feet to 4 feet 9 inches. They cannot be made much longer lest they should sag, as they are only supported at their extremities. If circular they are generally about 6½ to 8 inches in internal diameter. In nearly all American works they are circular, and from 8 to 9 inches in diameter. When elliptical the long axis is usually about 9 to 10 inches, and the short axis 6 to 7½ inches. The walls are from 1 inch to 1¼ inches thick. In the Silesian method the retorts are large and muffle-shaped, and generally of the following dimensions :—Length, 5 feet 3 inches to 6 feet 7 inches, breadth 6 to 8 inches, and height 1 foot 7½ inches to 2 feet 1½ inches.

In the Belgo-Silesian or Rhenish method the retorts are of an intermediate type. They are more or less elliptical in section, and vary in length from

4 feet 3 inches to 5 feet 5½ inches ; in their long axis from 9·8 to 11·8 inches and in their short axis 6·7 to 7 inches. Their walls are about 1¼ inches in thickness, except the back wall, which is 2 inches. Except in the Silesian method, the retorts are set in the furnace with an inclination downwards to the front wall to facilitate the removal of the spent charge, and also to allow of any fused silicates or other material to run down to the front and cooler part of the retort, and so diminish their corrosive action.

The material for the construction of the retorts must be extremely refractory. It consists usually of a mixture of one or more fire-clays with burnt clay, ground old retorts, and coke.

The composition of the mixture of clays varies at different works.

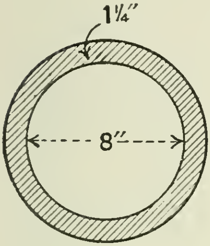
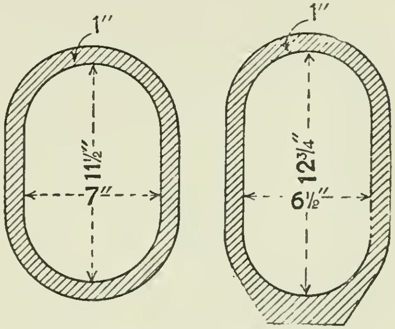


Fig. 188.—Belgian Retorts. Sections.



Belgo-Silesian Retorts. Sections.

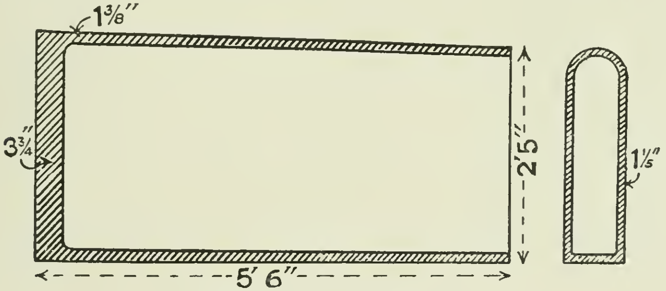


Fig. 189.—Silesian Retort.

Theoretically it should have an excess of silica if the minerals treated have a gangue rich in quartz ; if, however, as is often the case, the gangue of the mineral is basic, the clay should, on the contrary, be rich in alumina.

In practice, however, on account of the variety of the ores supplied to most works, a mixture of a medium character, which has been found by experience to be suitable for charges of a definite composition, is adhered to, and the ores are, as far as possible, mixed in the proportions required to give charges of that composition.

The retorts are made both by hand and by hydraulic machines, the latter being greatly superior to the former, as they are denser, and on this account more durable and less permeable by zinc vapour.

When hydraulic machines are used the mixture for the construction of the retort is either stamped or pressed by a machine into the form of a cylindrical mass, which is then squirted in a hydraulic press in a similar manner to that in which earthenware drain pipes are made.

Good retorts thus made last from 30 to 40 days.

In order to prevent or diminish the corrosion when ores high in iron or lead are treated, retorts with a lining of chromite, carborundum, or magnesite have been made recently, but it is doubtful whether their extra durability compensates for their extra cost.

The retorts are dried very gradually in chambers heated to a moderate temperature, and before being placed in the distillation furnace they are annealed in kilns, from which they are taken to the furnaces. The condensers are of the forms shown in Fig. 190, and need not be of such refractory clay as the retorts. They are coated before use with a wash of milk of lime, to facilitate the removal of adherent material.

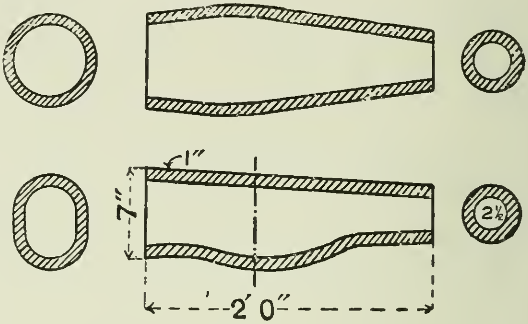


Fig. 190.—Condensers.

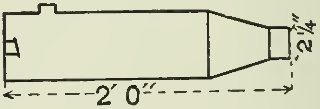


Fig. 191.—Prolongs.

The Nozzles or Prolongs.—A simple form in use in South Wales is merely a tube, sometimes a cone, of sheet iron fitted over the mouth of the condenser.

One of the shape of a long sheet-iron canister is common in America. It is pierced near its extremity with a small hole, which allows the escape of the gases (Fig. 191).[*] The object of the nozzles is to collect the zinc "fume"—*i.e.*, the portion of the zinc vapour which does not condense as fluid zinc, but as finely divided metal mixed with ZnO—and also to prevent air from entering the condensers and oxidizing the metal.

The Belgian Method of Zinc Extraction.—The furnace consists of a narrow vertical arched chamber, in which the retorts are arranged in parallel rows one above another, supported only at both ends in order that they may be surrounded by flame. As high furnaces present considerable difficulties in manipulation, most have now only four to seven rows of retorts. In America the furnaces for the most part are built back to back, forming a block, and having 224 retorts arranged in seven rows of 16 each—*i.e.*, 112 per side (*Ingalls*). There is a fire-place at the bottom of each chamber. It extends from one end to the other, and is furnished with two long grates, which are separated in the middle by a transverse wall rising only a few inches above the bed of fuel. Each end is fitted with a fire-door. The fire-place is made deep, sometimes with a step-grate, to cause partial gasification of the coal, but in the Eastern States of America, where anthracite is used, a closed grate with a blast is employed. Coal-firing has, however, been largely abandoned in favour of gas-firing.

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[*] Ingalls, *op. cit.*, p. 387.

A typical Belgian furnace, which is in use in the Western States of America, is illustrated in Fig. 192. The front is formed of horizontal cast-iron plates, with uprights between them, so placed as to form a series of rectangular compartments in each of which the mouths of generally two retorts are contained. The ironwork is protected from the heat of the furnace by horizontal and vertical fire-clay slabs. In the back wall of the furnace is a series of ledges, upon which the closed ends of the retorts are supported.

The mouths of the retorts are luted into the compartments with fire-clay and broken bricks, to prevent access of air to the interior of the furnace. There are two openings in the arch of each chamber communicating with a horizontal flue, by which the furnace gases are led to the chimney at each end of the block. The whole structure is firmly braced together with buck-stays and tie-rods. In the floor in front of the furnaces is a series of pits and shoots, into which the residue from each retort is raked, and thus passes into the ashpit.

The modern tendency, both in Belgium and America, is toward reducing the height of the furnaces to five or even four or three rows of retorts, thus following the Rhenish practice, especially when gas is employed as fuel. In modern Belgian furnaces gas firing has been largely adopted, the gas being supplied from the producers built either in or near the furnaces, or entirely independent of them. Until recently the natural gas in Kansas and Oklahama was largely used as fuel in spelter works, but owing to its partial exhaustion the works in those districts have been or are being transferred to other places where coal is cheap.

Firing with powdered coal has been tried at Cherryvale, Kansas, but the experiments were not continued, although the economy resulting from its use was demonstrated. Firing with oil is in regular operation at these works both for the roasting and the distillation furnaces. In the most recent practice the furnaces have independent gas producers, also regenerative chambers; in the older furnaces, in Belgium, however, the producers are chiefly of the Boetius type.

The Siemens regenerative system has not found any general application with the purely Belgian type of furnace, not, however, because of its inapplicability to the type, but because in building improved furnaces there is a tendency to abandon the Belgian for the Rhenish form (*Ingalls*). So that, where the Siemens system is in use, the furnaces are generally only three to five retorts high, and closely approach the Rhenish type, as with the higher furnace it was difficult to obtain a regular temperature throughout the chamber. A typical Siemens-Rhenish zinc distillation furnace in use in Belgium is illustrated in Figs. 193 and 194.*

The gas and air enter the regenerative chambers on one side of the furnace, and mix in the flue above them, the burning gas then passing up through the rows of retorts on that side and down through the rows of retorts on the other to the regenerative chambers below, and thence to the chimney stack.

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* Ingalls, *op. cit.*, pp. 459, 460.

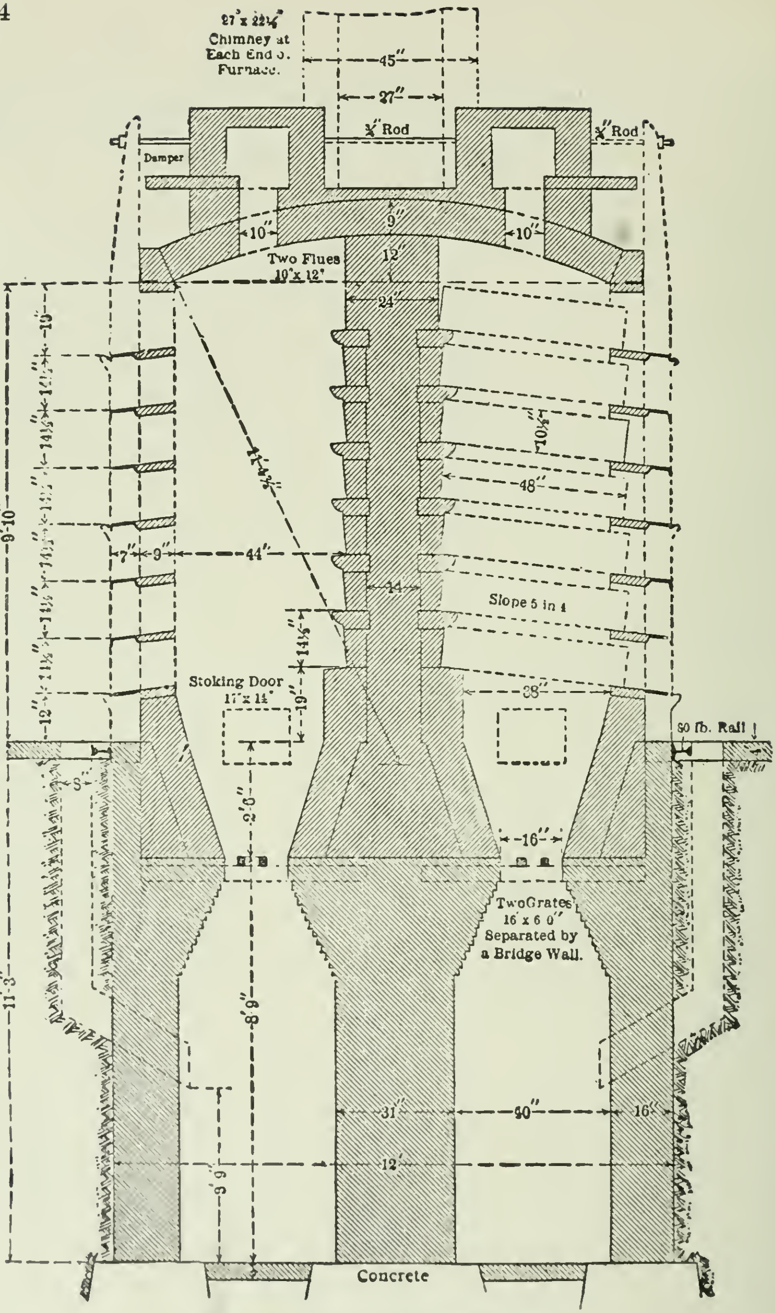
27" x 22¼"
Chimney at Each End o. Furnace.
45"
27"
¾" Rod
¾" Rod
Damper
10"
9"
10"
12"
Two Flues 10" x 12"
24"
10"
14½"
14½"
14½"
14½"
14½"
11½"
12"
9'-10"
11'-4½"
10½"
48"
7"
9"
44"
14"
Slope 5 in 4
14½"
19"
Stoking Door 17" x 14"
38"
80 lb. Rail
8"
2'-0"
16"
Two Grates 16' x 6' 0" Separated by a Bridge Wall.
11'-3"
8'-9"
6'-9"
31"
40"
16"
12'
Concrete

Fig. 192.—American-Belgian Furnace.*

* Ingalls, *op. cit.*, p. 434.

The direction of the currents of gas and air is reversed about every half hour by valves, not shown in the figures.

In the furnace known as the Neureuther-Siemens furnace, several of which are in use in America, uniformity of temperature in Belgian furnaces with five rows of retorts is aimed at. The furnace has the usual Siemens regenerators below, as in Fig. 193, but the mixed gas and air do not pass under the

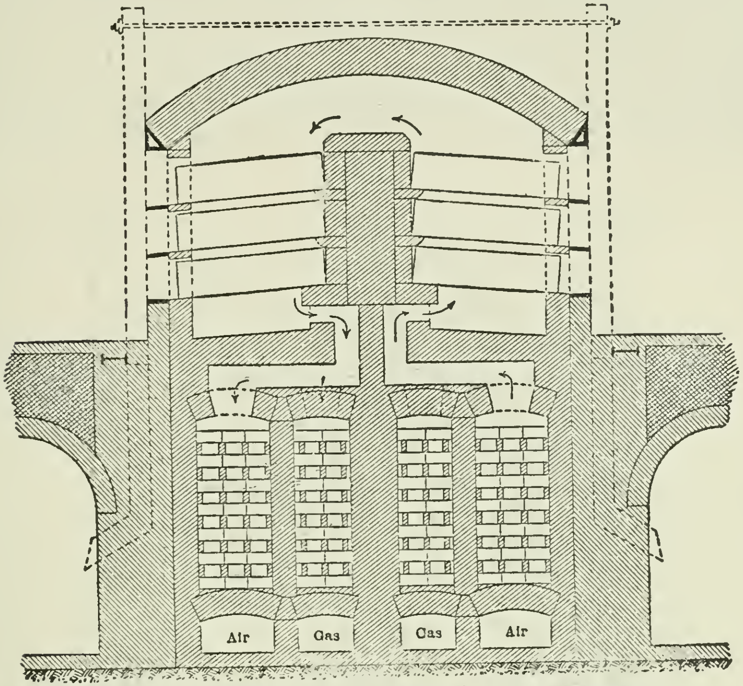

Fig 193.—Siemens-Rhenish Furnace. Transverse Section.

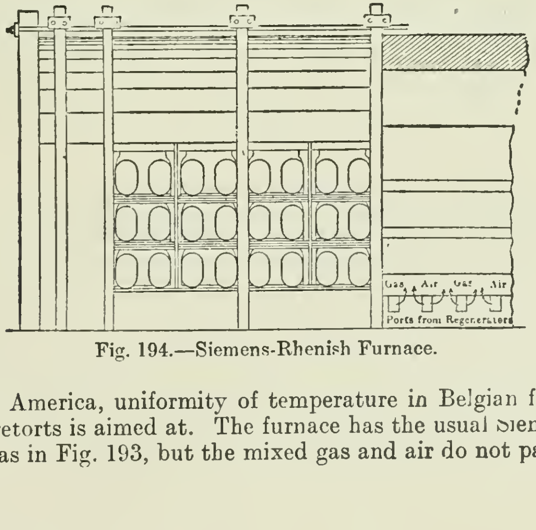

Fig. 194.—Siemens-Rhenish Furnace.

lowest row of retorts, but up channels in the median wall, from which they are discharged into the furnace chamber at different levels. The heating of the different rows of retorts is thus more regular.

A typical example of a modern American gas-fired furnace is shown in section in Fig. 195.* It is one of a block of four at the recently erected spelter works at Langeloth, near Pittsburg, Pennsylvania, each having 434 circular retorts 8 inches diameter on each side. Each furnace is fired with gas from a producer. At the end, where the gas enters the furnace, the middle wall stops short of the end wall, and is there reduced to a thin edge, the purpose being to divide the gas between the two combustion chambers.

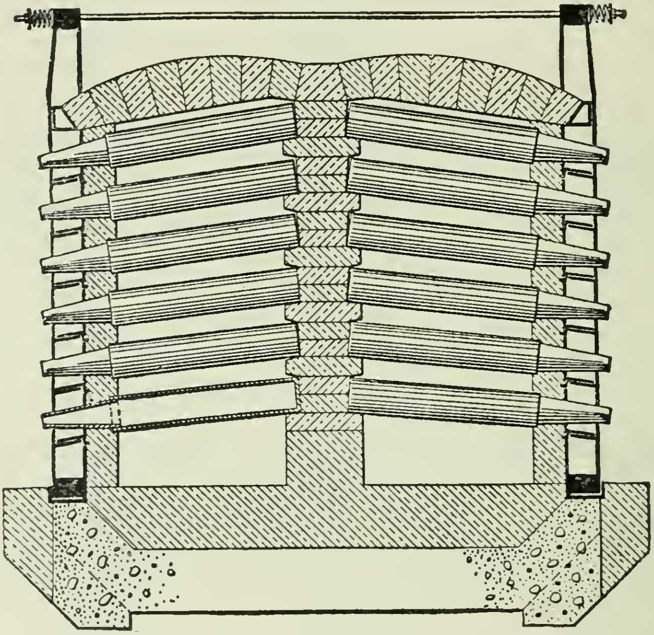

Fig. 195.—Transverse Section of Distillation Furance, Langeloth, Pennsylvania.

At the chimney end there is a wall of chequer-work, by the closing of the openings of which, the current of the combustion gases may be controlled to some extent. The gases on their way to the chimney stack raise steam in a tubular boiler of 525 H.P. The air for the combustion of the gas is supplied by a Sirocco fan through an air-main which runs along the top of the furnace. From this main, branches descend on each front and deliver the air into the furnace through ports between every section of 24 retorts.

A type of distilling furnace introduced at the works of the English

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* *Eng. and Min. Journ.*, Dec. 8th, 1914.

Crown Spelter Company, Swansea, by E. Ruck, general manager of the company, is shown in Fig. 195*a*.*

The specially interesting feature of this furnace is the provision of gas and air conduits in the front wall of the furnace, which is intended to improve the heating of the front ends of the retorts. In the figure, A shows the air regenerators, and B the gas regenerators. Part of the hot gases from the regenerators passes upward over the retorts C, D, E, through passages at G, and descends through the other half of the heating chamber, while the front ends of the retorts in the second tier are heated by the gases passing through the flues H, J in the direction of the arrows. These passages have outlets in the neighbourhood of the front ends of the retorts. In the distillation of 754 tons of ore, averaging 46·54 per cent. zinc, the coal consumption was 1·15 tons per ton of ore.

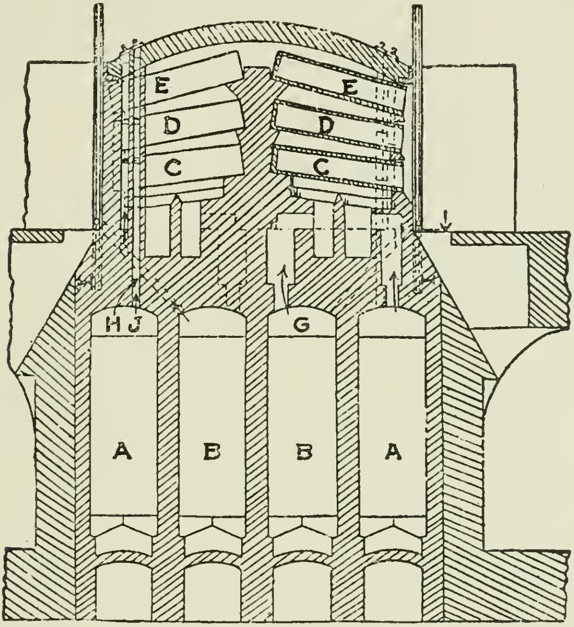

Fig. 195*a*.—Transverse Section of Ruck Furnace.

The Silesian Method.—The chief feature of the old Silesian method was the employment of large retorts in the form of muffles set in one row. These large muffles were indeed suitable for the treatment of the local poor, but easily reducible calamine, but since the deposits of this ore have become more and more exhausted, and roasted zinc blende requiring a higher temperature has to form a great part of the charge, the old furnaces have been largely replaced by those with two or three rows of retorts, either muffle-shaped or elliptical, and of moderate size. The tendency is thus to approach the Rhenish method, also to employ gas as fuel with or without regenerative chambers, so that the old Silesian furnaces and muffles are becoming obsolete. The following are types of modern practice :—

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* *Eng and Min. Journ.*, Feb. 1919

At the new works at Hohenlohe, the retorts, which are elliptical in cross-section, are 4 feet 7 inches long, about 1 foot high, and 7 inches wide, and are set in two rows. The furnace, which is gas-fired, is a double one, each side having 48 retorts.

At the Kunigunde Works the retorts are also elliptical. Their dimensions are—length 5 feet 2 inches, height 1 foot 3 inches, width about 8 inches. They are set in three rows in a gas-fired double furnace, 72 being on each side.

Furnaces of the Siemens reversing type with three rows of retorts are now in most frequent use in Upper Silesia.

The Belgo-Silesian or Rhenish Method.—The Rhenish method is a modification developed by a combination of the best features of the Belgian and Silesian.

The furnaces are all double, often with 60, or in the larger furnaces 120, retorts on each side arranged in three rows, but there are many variations. Those of recent construction are all gas-fired, and are furnished with regenerative chambers. In the large furnaces, the retorts in the lower rows are 4 feet 1 inch to 4 feet 3 inches in length, and in the upper row 5 feet 3 inches. They are elliptical in section, $10\frac{1}{4}$ to $11\frac{3}{4}$ inches high and about 7 inches wide. Four Siemens producers supply the gas to each furnace. Other producers, however, are employed in some works.

The gas and air, after passing respectively through the first pair of regenerators, enter the furnace through apertures in the bridge between the two chambers, the flame, after heating the retorts, then descends through similar apertures into the other pair of regenerators, and thence to the chimney stack (see Fig. 193). The direction of the gas and air is reversed about every half-hour.

The charge for a furnace of 240 retorts is usually about 10 tons of ore, containing 40 to 55 per cent. zinc with about 10 cwts. of furnace residues and about $4\frac{3}{4}$ tons of coal as reducing agent.

In the Rhine provinces there are also gas-fired furnaces without regenerators. A typical furnace of this type, with 108 elliptical retorts on each side, arranged in three rows, has a Boetius gas producer built into each end.

At one of the typical spelter works, in South Wales, furnaces of the Rhenish type with gas as fuel and regenerative chambers for gas and air are employed. The retorts are arranged in two rows, and are of the following dimensions :—Length 4 feet 6 inches to about 5 feet 6 inches, the longer being used when the back walls of the furnaces are worn ; height 11 inches ; width 7 inches. They are all made in a hydraulic press. The furnaces are double, and have 77 retorts on each side. The condensers are of the common form (Fig. 190), but the prolongs, which are simply sheet-iron pipes, are unusually long.

The gas is generated in producers of the Siemens type.

Calcined calamine, roasted blende, with the usual smelting by-products and ground anthracite as the reducing agent, form the smelting charges. The blend is first dried in a straight-line reverberatory furnace with mechanical rabbles, after which it is ground in a ball mill, and then roasted in a Merton furnace.

The Process of Distillation—*Preparation of the Charges.*—At the present time the zinc ores treated in America consist largely of concentrate from low-grade sulphide ores, of which vast deposits are being exploited.

At the Media Mill, Webb City, Missouri, a concentrate containing about 59 per cent. Zn is profitably obtained from an ore that yields barely more than 2 per cent. zinc sulphide.*

The concentrate obtained by flotation, the production of which is steadily increasing, is giving rise to great difficulties in smelting. It is excessively fine, ranging from 80 to less than 200 mesh, and is hence difficult to roast without excessive loss. When roasted it is difficult to charge, and occupies more space in the retorts than ordinary ore. Further, it is liable to be blown out of the retorts soon after charging. It is extremely desirable that the sulphur in the charge should be as low as possible, in order to diminish the amount of zinc which will remain unreduced in the residue in the retorts. In this connection it should be noted that, according to the experiments of Prost, the effects of an imperfect roasting of ferruginous blendes is less marked than in the case of plumbiferous blendes, probably owing to the decomposing action of reduced iron on zinc sulphide.

The calcined or roasted ores are mixed, as far as possible, so that the residue left in the retorts after distillation shall not be fused or agglomerated, but can be easily raked out. The formation of fusible silicates must be avoided also, on account of their corrosive action on the retorts. Hence the proportions of iron to silica in the charge must be limited.

In Europe the percentage of iron is not allowed to exceed 7 to 8 per cent., whilst in America few smelters care to have more than 2½ per cent., yet the presence of some iron is desirable. At certain American works, Leadville ore containing 20 per cent. of iron is said to have been smelted without admixture of any other ore,† but in this case the percentage of silica must have been low.

Lead is admissible up to 10 per cent. In fact, ores containing sufficient lead and silver to yield a residue which can be sold to lead smelters are now preferred by German firms.

Now that Broken Hill concentrate (p. 464) is available in vast quantities, the recovery of the lead as a by-product in zinc smelting is imperative, and in this connection it may be mentioned that Mr. Moulden, of the Seaton Carew Works, Hartlepool, who has roasted and distilled some thousands of tons of this ore containing from 14 to even 20 per cent. Pb, states ‡ "that with due exercise of care and the selection of appropriate retort materials, the old difficulties may be overcome to such a degree as to allow of entirely profitable commercial working" (see also p. 495).

The reducing agent is coal, anthracite, or a mixture of coal and coke. Whichever is used, it should be low in ash, contain but little sulphur, and the ash should not be fusible. It is mixed with the ores in the proportion of 40 to 45 or even 60 per cent. This is three or four times the quantity required by theory. A part is consumed by acting on the iron and lead oxides, etc., part is required to prevent agglomeration of the residue left after distillation, but the chief object of the excess is to convert any CO_2 formed into CO, thus—

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* *Eng. and Min. Journ.*, April, 1916.

† *Min. Ind.*, 1907, p. 928.

‡ *Journ. Royal Society of Arts, May*, 1916, p. 507.

$$CO_2 + C = 2CO.$$

As has already been pointed out, CO_2 oxidizes the vapour of zinc.

The fineness of the materials composing the charge is important, thus for roasted blende the particles should not exceed 2 mm., for calcined calamine and the reducing agent about 5 to 6 mm.

The charges are mixed in mixing troughs, or in special mixing machines, and are usually slightly moistened with water before being introduced into the retorts. This water, however, is driven off before the zinc begins to distil, so that its vapour does not dilute the zinc vapour or oxidize it. The ore in a charge generally contains about 45 to 50 per cent. of zinc, the weight of a charge varying with the size of the retorts. Thus for Belgian retorts in the United States it is about 60 lbs. of ore + by-products, exclusive of the reduction material, and for Belgo-Silesian in Europe 75 to 90 lbs.

Distillation of the Charge.—The retorts, after the residue from the previous charge has been removed, are filled with the mixed ore and coal by means of scoop-shaped shovels, those in the hottest parts of the furnace often receiving less easily reducible charges than the others. A small rod is then sometimes thrust through the charge at the top to make a hole for the escape of the first gas (*Ingalls*).

Both the operations of cleaning out and charging entail much labour, so that charging and cleaning machines have been introduced in several European works, but they are necessarily cumbersome, and the economy gained has not yet been found to be sufficient for their general installation in the United States.

In American works the furnaces are set in parallel and not in a line as in Europe, and this is unfavourable to the use of the machines, the National Zinc Company have, however, introduced with success a Saeger charging machine in their works at Bartlesville, Oklahoma (see p. 494).

After the retorts have been filled the condensers are set in their mouths, and carefully luted in with fire-clay. The temperature of the furnace is then raised, and after a time CO is given off, and burns with a blue flame at the mouths of the condensers, which have been partially closed with easily removable brasque, sometimes with a little of the charge. As soon as the flame shows indications of zinc, the brasque is removed, and the nozzles or prolongs are put on.

The first zinc vapours which come off do not, on account of their dilution, condense to fluid zinc, but to zinc fume, a mixture of finely divided zinc and zinc oxide. After a time they condense to metal, which remains fluid in the condensers. The condensed zinc is removed from the condensers generally three times during the working of the charge by taking off the prolongs and dipping it out with spoon-like ladles, or raking it with small rakes into an iron pot or kettle held below each condenser. In some few works the zinc is only removed at the end of the operation.

As soon as the kettle is full coke or anthracite dust is thrown on the surface of the molten zinc, and when this has been skimmed off the metal is cast into the usual slabs or plates in cast-iron moulds.

Towards the end of the process the temperature is further raised, and when no more zinc comes over, the prolongs and condensers are removed and cleaned, the retorts scraped out, broken retorts replaced, and the furnace made ready for the next charge. The operation occupies twenty-four hours both in the modern Belgian and Belgo-Silesian systems. The mean duration of a retort is about 20 to 25 days.

In America the zinc which distils over first is often kept apart and sold for the manufacture of the best brass, as it contains but little iron and less lead than the subsequent metal.

The yield of zinc in Europe from a 40 or 50 per cent. ore under the most favourable conditions rarely exceeds 90 per cent. of the metal present.

Mr. Ingalls * states as a broad generalization that the American smelter uses about 2 to 2½ tons of coal and 2 or 3 man-days of labour per ton of raw sulphide ore, and extracts about 84 to 88 per cent. of the zinc in the ore, and if he treats lead-bearing ore, he may recover 50 to 60 per cent. of lead. Whilst the European smelter uses about 1¼ to 1¾ tons of coal and 3 to 3½ man-days of labour and extracts about 88 to 90 per cent. of the zinc in the ore and about 50 to 70 per cent. of the lead.

The loss of zinc is due to various causes, of which the following are the most important :—

1. Zinc remaining in the residue. This is the chief cause, as under the most favourable conditions this residue rarely contains less than 3 to 5 per cent. zinc, and usually much more.

The metal is chiefly present in the form of sulphide, hence the importance of thorough roasting of blende. Some may also exist as unreduced silicate or even oxide if the temperature of the furnace has not been properly maintained.

Roasting at too low a temperature will leave zinc sulphate in the charge, and this by reduction by the coal will cause the formation of zinc sulphide in the retort.

Roasting at too high a temperature will also cause the retort residues to be high in zinc.

2. Absorption by the retorts. Old retorts will sometimes contain 7 or 8 per cent. of zinc.

3. Permeation of the retorts by zinc vapour. This has been greatly diminished by the introduction of retorts by hydraulic pressure. With the same object, in some works the retorts are coated both inside and outside with a glaze.

4. Escape of zinc vapour when the condensers are opened for the removal of the metal, and when they are removed at the end of the process.

5. Escape of zinc vapour owing to cracked and broken retorts.

This cause of loss has been much lessened by the use of machine-made retorts and gas-firing.

6. The condensation of part of the zinc vapour in the form of zinc fume (blue powder), which will usually amount to about 5 per cent. or more of the weight of zinc obtained as metal.

The consumption of fuel in the distillation process is large, and is greater in the Belgian than in Belgo-Silesian, and in coal-fired than in gas-fired furnaces. Coal-fired furnaces are, however, being displaced by those with gas-firing.

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* *Eng. and Min. Journ.*, Oct. 1915.

In modern gas-fired Belgian furnaces about 1·6 tons of coal is required per ton of ore treated, whilst for Belgo-Silesian and Rhenish furnaces the average is about 1·1 to 1·2 tons, but much depends on the quality of the coal supplied to the producers.

" One of the most revolutionary ideas in the metallurgy of zinc has been tested at Bartlesville, Okla. The idea was to distil large tonnages of roasted ore in retorts, using only relatively small quantities of reducing fuel and employing relatively unskilled labour. The metallurgist is contented with a low extraction of zinc, say 60 per cent., but is careful not to burn any zinc during this operation. The retort residues, high in both lead and zinc, are burned in Wetherill grate furnaces for the production of oxide of zinc, and there is thus obtained a zinc extraction relatively high by rougher and less expensive methods than the present." *

" Such a procedure should increase the capacity of the distilling furnace and result in longer life of retorts, as they should not require to be submitted to the high final temperature necessary to drive off the last units of zinc" (*Picard*).

The products of the distillation process are :—

Crude zinc. Zinc fume (blue powder). Residue.

Crude Zinc.—The zinc obtained by the distillation process in America is generally sufficiently pure for industrial uses. In Europe, however, it is often impure. The chief impurities are lead and iron, the former sometimes reaching 2·0 to 3·5, and the latter 0·3 or more per cent. Cadmium, too, is frequently present in small amounts, also arsenic and antimony. The last two elements usually occur in only minute quantities.

Refining.—In order to remove the excess of lead and iron, the crude metal is treated by a refining process, which is based on the liquation of zinc from these metals, when it is kept molten for some time as near its melting point as possible. At this temperature zinc will only retain about 1·0 to 1·1 per cent. of lead in solution, the excess settling to the bottom of the furnace alloyed with some zinc. Under no conditions can the lead be reduced below 0·8 per cent. The iron also settles as a zinc-iron alloy, forming a layer above the lead.

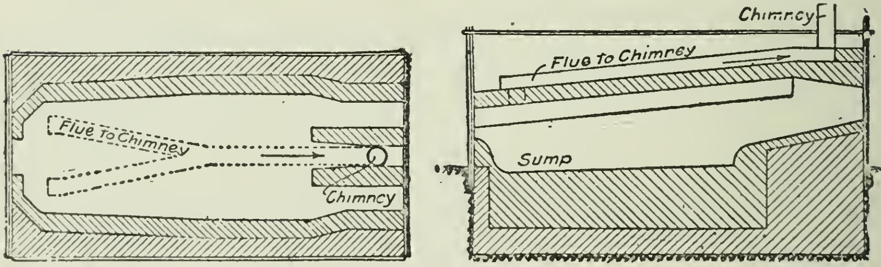

Fig. 196.—Zinc Refining Furnace.

The operation of refining is carried out in reverberatory furnaces, of which there are several kinds, all constructed on the same principles. A typical form, which will take a charge of about 20 tons, is shown in Fig. 196.† The hearth, which is of fire-clay firmly beaten down, measures about 13 feet by 6 feet, and slopes downward from the fire-bridge to the lading door.

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* W. R. Ingalls, *Eng. and Min Journ.*, Jan. 1918. † *Journ. Inst. Met.*, vol. ii., p. 232.

Within the lading door a cast-iron plate, projecting down from the roof and dipping into the zinc, is sometimes fitted, to prevent air from passing into the interior of the furnace and oxidizing the metal. For the same reason the flame from the fire-place must be as reducing as possible.

The crude zinc is charged in through a door near the fire-bridge, and melted down very slowly, the fire being kept low and the flame reducing.

If the temperature is too high the zinc will retain much lead, as the solubility of lead in zinc rises with the temperature; at 650° C. it will dissolve 5 to 6 per cent.

When the charge is molten, which requires about two days, the scum which has formed on the surface is removed with perforated ladles, or is skimmed off and about one-third of the zinc in the furnace is laded out, at the lowest possible temperature, into iron moulds, in which it is cast either into cakes for sale or slabs for rolling. The moulds in the best works are set on a rotating table in front of the lading door.

An equal quantity of crude zinc is then charged into the furnace, and when molten and settled the lading is repeated. The lead which separates and collects at the bottom of the furnace contains about 6 per cent. of zinc. The iron in the form of a zinc-iron alloy also settles down and floats on the lead as a pasty mass of so-called " hard " zinc, containing 15 to 20 per cent. of iron. The lead bottoms are allowed to accumulate for seven or eight days, when they are best removed in the following manner :—

A wide clay tube open at both ends, with its lower end scalloped and temporarily closed with a plug of clay, is plunged to the bottom of the layer of lead and fixed. The plug is then broken out, and the lead rising in the tube is taken out with ladles. The layer of ferruginous zinc is generally allowed to accumulate until the refining campaign is over, when the zinc is all laded out and the pasty mass removed with perforated ladles. The lead containing zinc can be used in the Parkes process for the desilverization of lead, or the lead can be refined by burning off the zinc.

The " hard " zinc can be redistilled or sold for the manufacture of sterro-metal.

Two methods are now extensively used for refining zinc by redistillation.* The older method makes use of an ordinary smelting furnace block ; the later method, invented by C. A. H. de Saulles, uses a single furnace with the back wall exposed. The retorts are inclined about 7 inches in their length and extended through the back wall 4 to 5 inches.

An opening is provided at the top of the projecting butt-end, through which the retort is charged with molten spelter ; at the bottom of the butt-end a small opening is provided through which the leady bottoms are tapped out ; both openings are tightly closed with clay, except when charging and tapping. The condenser used is of the ordinary shape and size, and is clayed into the retort. The furnaces are fired with gas and coal, Belgian style, using a thin flame and natural draught. The furnaces are 2, 3, and 4 rows high, and contain from 80 to 200 retorts. Each retort distilling furnace is served by one 25-ton remelting furnace and one 25-ton equalizing furnace.

The three furnaces are built close together and comprise a redistillation unit. One equalizing furnace may be dispensed with by operating two units together.

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* *Min. Mag.*, Jan. 1918. Abstract of paper by L. E. Wemple read before the American Institute of Mining Engineers.

The spelter to be redistilled is melted down in the remelting furnace, where a large part of the lead settles out. After settling, the metal is drawn off from the top of the molten bath into a ladle and fed into the butt-end of the retort. The retorts are charged once in 24 hours, the two top rows at 7 a.m., and the two bottom rows at 7 p.m. The charge openings are closed with clay packing immediately after pouring in the metal, and distillation of the zinc begins with a minimum delay as the furnace is kept at a uniform heat. The metals are carefully maintained at the temperature at which zinc volatilizes, but below that at which lead volatilizes. The condensers are drawn every four hours into a ladle, by which the redistilled zinc is taken to the equalizing furnace.

The equalizing furnace serves the purpose of cooling the over-heated metal from the condensers, and blends the metal from the various draws into lots of uniform spelter, which are then cast into the usual plates or slabs. The leady metal is tapped from the retorts 24 hours after charging, about 20 lbs. being removed from each retort.

Every two or three weeks the accumulation of lead settling in the bottom of the remelting furnace is tapped out through a bottom tap, cast into moulds, and shipped to lead refiners.

The spelter ordinarily treated contains 1·5 to 3 per cent. lead, 0·03 to 1·0 per cent. iron, and 0·03 to 0·07 per cent. cadmium. The redistilled spelter contains from 0·03 to 0·12 per cent. lead, 0·008 to 0·012 per cent. iron, and 0·03 to 0·07 per cent. cadmium.

Zinc Fume.—In America zinc fume is called " blue powder." As already pointed out, it consists of a mixture of zinc in fine powder with zinc oxide and a little cadmium oxide. It also contains lead up to 2·5 per cent. The zinc existing as metal ranges from about 85·0 to 90·0 per cent., and the zinc oxide from 8·0 to 13·0 per cent. In some works it is added to the charges of the retorts in the cooler parts of the furnaces, but when it contains sufficient cadmium it is set apart for the extraction of that metal. It is sold by some smelters in Europe to indigo works as a reducing agent, and it has also been employed in the Merrill process for precipitating gold from cyanide solutions.

Residue from Retorts.—The composition of the residue naturally depends on the composition of the ores treated. When the ores contain much lead and silver, practically the whole of the silver and most of the lead will be found in the residues. They are then sold, sometimes after concentration by grinding, screening, and jigging, to lead smelters, to whom they are also valuable for the iron they contain.

At the Edgar Zinc Company's works, the residues after screening through ¼-inch mesh are mixed with 20 per cent. of fresh coal and used as fuel under steam boilers. Ten boilers are thus fired. At some works, when they contain only a little silver and lead, they are burnt on Wetherill grates, and the zinc they contain is recovered as oxide.

Charging and Discharging Machines.—The Saeger machine is mounted on a truck of 11-foot gauge, and consists of a hopper bin with a capacity sufficient for charging half of one side of a block of furnaces. From the bin the charge passes through pipe conduits to eight spiral feeding devices, which are so placed as to enter and charge eight retorts arranged in two tiers of four. In charging, the charging spouts are inserted into the retorts to within 5 or 6 inches of the back, when the charge is forced in, by a spiral feed through the spouts. As the retorts become filled the spouts are gradually withdrawn, and when the retorts are full, an automatic cut-off stops the feed. The machine is operated by electricity. After the retorts are charged, the machine is moved to the next eight, and the operation is repeated along the whole length of the furnace. The machine is said to charge the retorts better than can be done by hand, and in less than half the time.

The Simmonds retort-discharging machine has also been introduced at two works in Oklahoma, and one in Colorado, and is said to operate satisfactorily. The machine is mounted on a truck which runs along rails in front of the furnace. The discharging mechanism consists of a series of bars, each carrying an endless chain fitted with scrapers. To discharge the retorts it is run in front of a vertical tier, and the chain of scrapers set in motion. The residue scraped out of the retorts falls down a series of shoots, one of which is provided for each bar, and is thus deflected from the mechanism working on the retorts lower down. The scraper-chains are sprayed with water to keep them cool. After one tier of retorts has been discharged, the machine is carried to the next tier, which is treated in the same manner The machine is said to discharge the residues in one-fourth the time required in the ordinary way.

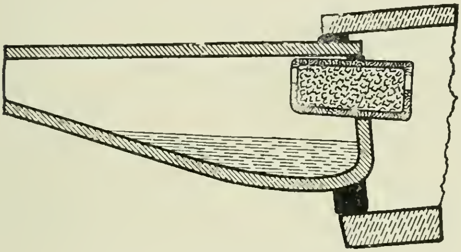

Fig. 197.—Zinc Fume Filter.*

Examples of Practice, supplementary to the Information in the Foregoing Pages.—Several methods have been proposed for treating roasted zinc - lead concentrate in ordinary zinc furnaces for the production of spelter containing but little lead and a residue suitable for lead smelters. A description of one of these used at Irvine, on the Firth of Clyde, was given by Mr. J. S. G. Primrose in the *Engineering and Mining Journal* of 27th August, 1911, of which the following is a brief summary :—

It consists in fitting a fire-clay tube filled with loosely packed refractory material,† such as chippings of burnt fire-clay, in the back of the condenser (Fig. 197), so that the vapour of zinc passes through it and is filtered. Any lead which may be present is retained in the material of the filter, zinc containing less than 0·6 per cent. lead condensing in the condenser.

Another method of producing a pure spelter from zinc-lead concentrate has been proposed by Sulman and Picard. It consists in briquetting the material with bituminous coal and pitch, and distilling the briquettes in an ordinary distillation furnace, when the carbonaceous residue is found to retain most of the lead in the metallic state, and is suitable for lead smelting. Very little lead is said to go over into spelter when the process is properly conducted.

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* *Journ. Inst. of Metals*, vol. ii., p. 268.

† The removal of lead by the filtration of zinc vapour was originally proposed by the Rev. E. W. Hopkins, who used charcoal or coke as the filtering medium. This process was described by C. O. Bannister, *Journ. Inst. of Metals*, vol. iii., p. 213.

The Deering Plant of the American Zinc, Lead, and Smelting Company *—It is situated in the Eastern Kansas gas belt. The works consist of a crushing and drying plant, three Zellweger roasting furnaces, and six blocks of retort furnaces for the reduction of the ore. There are also coal crushers, a laboratory, and a complete pottery for the manufacture of retorts and condensers. The plant has a capacity of between 600 and 700 tons of zinc ore per week, nearly all of it coming from the Joplin district. The production of spelter is 300 tons per week.

The roasting furnaces operate satisfactorily, reducing the sulphur contents of the ore from 30 per cent. to less than 1 per cent. From the roasting kilns the ore goes to the weighing room, where the proper amount for mixing is weighed out into cars.

From the weighing-room the ore is carried to the mix-house, where it is mixed with coal. This is done by bedding. The mixing pits are about 6 feet square and 2 feet deep, and are paved with brick. At one end is an iron grating along the entire end of the pit. Underneath this grating is a screw conveyor, which serves both as a mixer and as a conveyor to the furnace bins. A layer of coal is spread on the floor and covered with ore, and so on, until the pit is filled. The screw is then started, and the mixture is shovelled into the conveyor until the pit is empty, when the operation is completed.

The furnaces are built with their backs together, so that one central wall serves for two furnaces. There are 20 sections to a furnace, each containing 16 retorts, making 320 to the furnace, or 640 to the block. They are four tiers high instead of five, as in some gas smelteries. For other examples, see p. 497.

The furnaces are charged by hand.

The Doncra Zinc Works.†—These works have been erected in the neighbourhood of Pittsburg by the American Steel and Wire Company. The location of the plant is a specially favourable one, being an important centre of spelter consumption, a large consumer of sulphuric acid and lead, besides possessing a great supply of some of the best gas coal.

The ore treated at present is Australian concentrate. The roasting department comprises six Hegeler furnaces with seven hearths, each hearth being 80 feet long by 6 feet wide. Each furnace is supplied with gas for firing from a mechanical gas producer. The combustion gases on their way to the chimney pass through a U-pipe stove, in the pipes of which the air for the combustion of the firing gas is heated to about 400° C. This heating of the air has, however, been discontinued, as it gave rise to too high a temperature in the furnace, resulting in sintering of the ore. The furnace gases contain about 4½ per cent. of SO_2. They are raised to a content of about 8 per cent. by the burning of sulphur in the dust catcher attached to each furnace, and then pass to the Glover towers of the sulphuric acid department.

The roasted ore is taken by the overhead telpherage system, which extends through the entire works, to the storage bins of the mixing house. Here it is mixed with the necessary quantity of coal in hexagonal drums, the heads of which are slanted so that a cross-section through the shaft is of rhomboidal shape. By the revolution of the drums the charge receives, therefore, not only a peripheral mixing, but also a lateral shifting.

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* *Eng. and Min. Journ.*, Sept. 1910.

† W. R. Ingalls, *Eng. and Min. Journ.*, Oct. 1916, p. 648, *et seq.*

In the distillation department there are ten furnaces, each taking 912 retorts, 456 per side, arranged in six tiers. The retorts are cylindrical; 8 inches internal diameter and 52 inches long. Each furnace is fired with gas from two gas producers; the air for combustion being furnished by a Sirocco fan. At the far end of the furnace the products of combustion pass through a tubular boiler of 588 H.P., and then to a chimney constructed of concrete.

The retorts are made in hydraulic presses and dried in rooms heated by steam piping below the grated floors.

In the following table is given an outline of the equipment at three modern American Spelter Works:—

	Granby Mining and Smelting Co., St. Louis, Missouri.*	American Zinc and Chemical Co., Langeloth, Pennsylvania.†	American Steel and Wire Co., Donora Works, near Pittsburg.‡
Material treated, . .	Concentrate	Lump ore and concentrate	Australian concentrate
Roasting furnaces, . .	2 Hegeler (7 hearths)	2 Hegeler (7 hearths)	6 Hegeler (7 hearths)
,, size, .	77 ft. by 6 ft.	80 ft. by 6 ft. 1 in.	80 ft. by 6 ft. 1 in.
Sulphuric acid plant, .	Chamber process	Chamber process	Chamber process
Distillation furnaces, .	4 blocks	4 blocks	10 blocks
,, Fuel,	Producer gas	Producer gas	Producer gas
Retorts, ...	Circular	Circular, 8 ins. diameter	Circular, 8 ins. diameter
,, Number on each side of furnace block, . .	405	432	456
,, Arrangement, .	5 tiers	6 tiers	6 tiers

Port Pirie, South Australia.§—At the Port Pirie zinc works of the Broken Hill Proprietary Company at Port Pirie, the concentrate treated contains about 46 per cent. zinc, 8 per cent. lead, 30 per cent. sulphur, and 13 ozs. silver per ton. It is roasted in Hegeler furnaces fired with gas from Duff producers. The furnaces are 79 feet in length, with two tiers of seven hearths, each 6 feet wide, and each double furnace has a capacity of 48 tons per twenty-four hours. The plant comprises ten furnaces of the Rhenish type, each having two tiers of retorts back to back with three rows of 24 retorts in each tier, or 144 retorts on the whole furnace. The retorts, which are made by hydraulic pressure, are 5 feet 6 inches long and 13 inches by 7 inches in elliptical cross-section. The condensers are made in the same moulds as the retorts, being simply the latter cut in two. When the retorts are in position, their ends, which have been bevelled on the outside, are well smeared with clay and the condensers, with their ends bevelled in the opposite direction, forced up against them. There is a gas producer for each furnace, the air for combustion of the producer gas being pre-heated by forcing it, by means of a fan, through flues and round the furnace itself before reaching the burners. The latter, of which there are four, are built in the form of large Bunsen burners in the hearth of the furnace between the two tiers of retorts. They are 18 inches in diameter, with gas inlet, 9 inches diameter, at the bottom, and air ports at the side. A typical charge is 10,000 lbs. of roasted ore, 3,000 lbs. of coke, and 1,500 lbs. of coal, plus condenser chippings and oversized blue powder. After being mixed on the furnace floor the charge is put into the retorts through the condensers.

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* *Min. and Sc. Press*, Sept. 1914.

† *Eng. and Min. Journ.*, Dec. 1914.

‡ *Eng. and Min. Journ.*, Oct. 1916.

§ F. W. Reid, *Min. and Eng. Review*, Oct. 1913. (Abstract in *Min. and Sc. Press*, Nov. 1913.)

After charging the retorts, the ends of the condensers are stopped by luting on cast-iron tiles, lined with fire-clay on the inside, and provided with a hole for the outward passage of vapours. Over a projecting collar, surrounding the hole, is fitted the small end of a conical sheet iron " prolong," the other end of which is supported by a movable bar resting on brackets on the front of the furnace. The prolongs serve to collect blue powder. The carbon monoxide escapes at a small hole at the outer end of the prolong. When the prolongs have been fixed in position the furnace is fired and distillation allowed to proceed. The temperature is taken at hourly intervals by means of a Wanner pyrometer. It is raised gradually until it reaches a maximum of 1,325° to 1,350° C. An hour or two before the day shift comes on, the prolongs are removed and the contained blue powder collected. The furnace is then ready for tapping. The tile on the end of the condenser is removed, the molten zinc allowed to run into a cast-iron ladle placed to receive it, and the condenser thoroughly scraped to remove all zinc and dross.

Raking out the retort residues is the next operation. For this purpose counterbalanced sheet-iron aprons are pulled down in front of the furnace and rakes inserted through openings opposite the retorts. The residues, deflected by the apron, fall through an opening in the floor close to the front of the furnace, and run by a shoot into trucks below. They are sent to the lead blast furnace for recovery of the lead and silver contents.

The furnace is next tested for cracked retorts. This is done by simply turning on the gas, when cracks can be detected by the flame coming through into the interior of the retort. Damaged retorts are replaced by new ones, and re-charging is commenced. The cycle of operations on the furnaces occupies twenty-four hours.

The zinc recovery in spelter and marketable blue powder is said to range from 80 to 85 per cent.

The blue powder averages about 12 per cent. of the total furnace product, and is of very good quality, containing 92½ per cent. metallic zinc. It is screened through a 100-mesh screen, and boxed for export to San Francisco or Japan, its two markets.

The spelter contains 2 to 3 per cent. of lead. It is refined by liquation in a reverberatory furnace in the ordinary way, the charge being about 20 tons. The refined spelter contains less than 1 per cent. of lead and approximately 99 per cent. metallic zinc.

The Manufacture of Zinc White.—Zinc white is zinc oxide, which is manufactured on an extensive scale in the United States, especially in New Jersey and Pennsylvania, and is largely used as a white pigment instead of white lead, as it is not discoloured by sulphuretted hydrogen. It is also used in the rubber manufacture. The process of manufacture, which is termed the Wetherill process, from the name of its inventor, is in outline, as follows :—

The ore containing zinc is mixed with the reducing agent, ground anthracite, and spread over a layer of burning anthracite on the perforated grate of a kiln, through which a low blast from a fan is forced. The zinc distils off, and is oxidized at once by the CO_2 formed during the reduction of the ZnO, and by the air present.

The gaseous products carrying the zinc oxide are passed through a cooling flue or towers to a series of woollen bags in a " bag-house," where they are filtered and the oxide collected.

The ore treated is franklinite, an iron ore containing varying amounts of iron, manganese, and zinc (p. 463). About 27 per cent. of zinc is usually present, chiefly as willemite.

A considerable proportion of this mineral is, however, now separated by treating the ore by a reducing calcination followed by treatment by a magnetic separator, the result being a product poor in iron and rich in zinc, which can be distilled for spelter, so that the ore used for the manufacture of zinc white contains only about 18 per cent. of iron.

The residue, after the extraction of the zinc, is smelted for manganiferous pig iron or spiegeleisen.

At Coffeyville, Kansas,* a plant has been erected for the application of the Wetherill process to mixed zinc and lead ores.

The method is suitable for the treatment of zinc ores containing too much lead for the ordinary distillation process, and lead ores containing too much zinc for lead smelting ; the ores should contain, however, not less than 30 per cent. of lead and zinc combined.

The ores are mixed in such proportions that the pigment shall consist of about two-thirds zinc oxide and one-third lead sulphate and oxide. They are first roasted in MacDougall furnaces. The roasted ore after admixture with coal is treated in the same way as for the preparation of zinc oxide described above, and in similar furnaces. The fume, however, is first passed through a combustion chamber, in which any carbonaceous matter carried over is burnt out. There are no cooling or settling towers, but instead a sheet-iron flue, 600 to 700 feet long, which terminates in a small settling chamber, placed just before the bag-house. Here the cooled fume enters a suction fan, and is forced into the bags in the bag-house, the pigment being collected in the usual manner.

It has been proposed by Blum to use Huntington-Heberlein pots, instead of furnaces of the type described above, for the manufacture of zinc white from ores, and a small plant has been erected in Mexico for carrying out his proposal.

At the Palmerton plants of the New Jersey Zinc Company, Penn., the process is carried out as follows :—† The ores used are almost entirely concentrates from the company's mines at Franklin and at Stirling

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* *Min. and Sc. Press*, Oct. 1908.

† G. C. Stone, Paper read before the American Institute of Mining Engineers, *Eng. and Min. Journ.*, 1917, p. 508, *et seq.*

Hill, N.J. They consist of three products of the composition given below.

	Franklinite.	Half-half.	Dust.
	Per cent.	Per cent.	Per cent.
Zn,	18·2	18·4	17·6
Fe,	35·0	15·2	20·1
Mn,	12·8	12·2	8·9
SiO_2,	3·6	12·6	7·2

The franklinite is worked by itself and the residue smelted in blast furnaces for the production of spiegeleisen. The half-half and dust are mixed and the residue thrown away, as it contains too little Fe and Mn and too much SiO_2 to be a profitable smelting material. There are two distinct plants in the works—viz., the East plant and the West plant—but the furnaces and operations in both are similar. In the East plant there are 26 blocks of furnaces, all consisting of four furnaces each 19 feet 6½ inches by 5 feet 11½ inches. Each furnace has independent blast and three charge openings in the roof surmounted by hoppers ; also two outlet pipes, usually 20 to 22 inches in diameter, which lead up to a wide horizontal sheet-iron flue overhead. The hearth of each furnace consists of cast-iron plates perforated with conical holes 0·25 to 0·40 inch in diameter at the top and 1 inch diameter at the bottom. The holes are thus tapered to prevent them from being stopped up, as the air from the blower must pass freely through them.

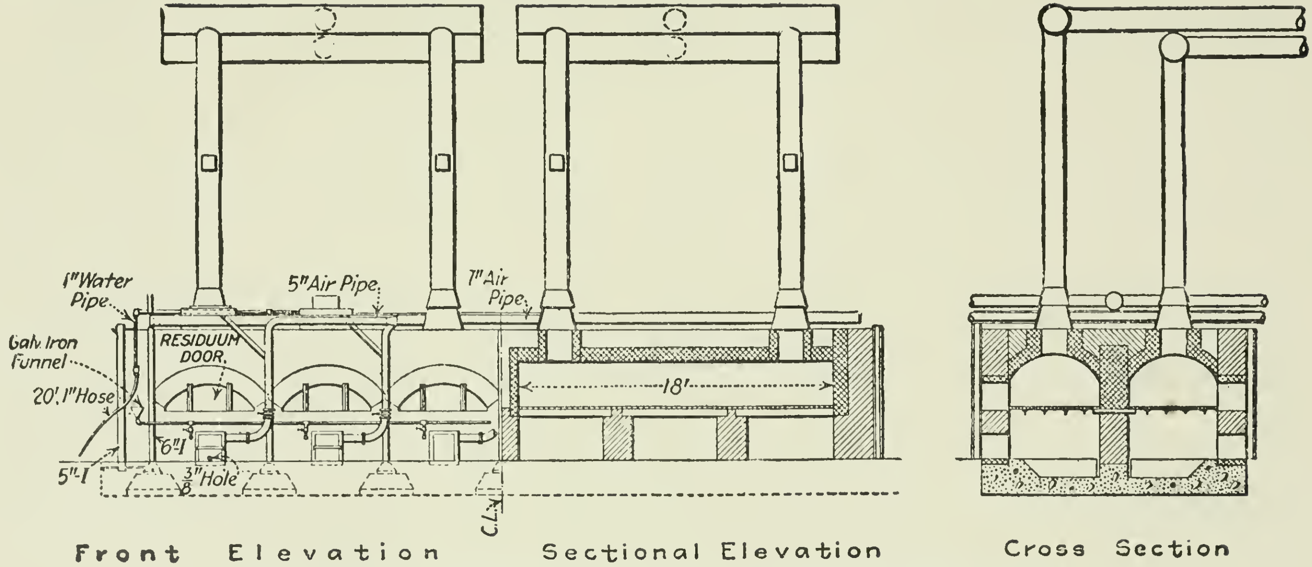
Each furnace works three charges in 24 hours. The different furnaces of the block are charged alternately at two-hour intervals in regular order. Charging in this way, there is always one furnace starting, one nearly finishing, and two working strongly, and the volume and temperature of the gases to be handled are nearly uniform at all times.

When the furnace is worked off, the dampers in the flues are closed, cutting it off from the bag room. The blast is shut off and the working doors taken down. Three men work on the furnace at once, each at a separate door. The loose material on the top of the charge is raked off and dropped on the floor close to the furnace. The clinker is then broken up by heavy slice bars and raked into hoppers under the floor.

When all the old charge has been removed and the furnace cleaned, the grate is covered as rapidly as possible with a thin layer of anthracite, the doors closed, and a light blast turned on. When the anthracite is burning brightly, the charge of ore mixed with the necessary amount of anthracite for reduction, usually about 80 to 100 per cent. of the weight of the ore, both being in coarse powder, is charged in through the hoppers and levelled. The charge, when spread over the furnace grates, will form a layer from 6 to 8 inches in depth.

The doors are then closed, the full blast turned on, and the furnace left to itself with occasional inspection to stop any blow-holes that may form.

With the large charges that are now worked, considerable time elapses


1" Water Pipe
Galv. Iron Funnel
20'. 1" Hose
5"-I
RESIDUUM DOOR.
6"-I
$\frac{3}{8}$" Hole
5" Air Pipe
7" Air Pipe
C.L.
18'

Front Elevation

Sectional Elevation

Cross Section

Figs. 198 and 199.—Eastern Furnace with Three Grates thrown longitudinally into one.

before any zinc vapour appears. When it does the dampers in the flues are reversed, sending the gases and oxides up the outlet pipes to the horizontal sheet-iron flue above. This flue has an outlet leading to the exhaust fan building, of which at the East plant there are two with ten fans each and one with six. From the exhaust fans the gases and oxide pass to the bag-house through sheet-iron pipes 3 feet in diameter, provided with numerous clean-out openings. Formerly the gases passed through a brick settling tower between the furnaces and exhaust fan, but this is now usually omitted as unnecessary.

The reactions are the same as in the ordinary distillation processes, but the zinc vapour is oxidized by the CO_2 and air present.

A standard type of the Eastern furnace is illustrated in Figs. 198 and 199.*

In the bag-house the gases enter a header at the top of the room, and from there pass to a series of parallel pipes, from the bottom of which the bags are connected to hoppers, four bags to each, with a single collecting bag tied to an outlet at the bottom of each hopper. At intervals the gases are shut off from two lines of pipe connecting with a single line of hoppers and the bags shaken. This pair of pipes is again connected to the main header and the next two lines shut off and the bags shaken. The bags used are all of heavy, closely woven cotton sheeting, 22 inches in diameter and about 40 feet long.

The zinc oxide produced at Palmerton is classified into five grades, two for the use of paint manufacturers, two for rubber, and an off grade that is reworked either for oxide or spelter.

About 86 per cent. of the zinc in the franklinite and 78 per cent. in the half-half and fines charge is obtained as oxide.

Extraction of Zinc from Slag.†—" A method in use at the lower Harz Mines of Oker is described in *Gluckauf* of February, 1910, by Dr. Pape. The ore is taken from the Rammelsberg ore bodies, the main varieties being lead ores with 9 per cent. lead and 20 per cent. zinc, and copper ores with from 1 to 15 per cent. copper and 1 to 20 per cent. zinc. These are treated in the ordinary way in blast furnaces, the lead ore after a sulphating roast to remove some of the zinc by leaching. The slags resulting have the composition ZnO, 22 to 27 per cent. ; FeO, 30 to 16 per cent. ; SiO_2, 23 to 9 per cent. ; and BaO, 7 to 26 per cent. About 42,000 lbs. of slag are formed every year. In the works erected for the purpose at Oker, as the result of a long series of trials, the slag is ground to 50 mesh, and then mixed with coke dust, and briquetted. The briquettes are reduced in a continuous reverberatory furnace, where the zinc after volatilization as metal is carried off as oxide by the flue gases. To precipitate this, the gases are passed through a stone channel to twelve water-tube boilers having their temperature reduced from 1,000° C. to about 280° C., and fans draw them through two iron towers to the bag-houses, before passing through which they are diluted with cold air to further reduce their temperature, to prevent injury to the bags. The oxide caught in the bags is the finest, and is sold as a pigment ; the rest is sent to a local works, where it is used for enriching poor zinc ores, in order that they may be treated by the Belgian process." According to Sulman, " Nearly

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* John F. Cregan, *Eng. and Min. Journ.*, Oct. 1917.

† Abstract in *Min. Mag.*, 1910, vol. ii., p. 228.

10,000 tons of metal are reported to have been thus produced, and 42,000 tons of zinc slags, besides low-grade ores, treated by this method in 1910." *

Electrolytic Zinc.†—Numerous attempts have been made during the last twenty or thirty years to use electrolytic methods for the extraction of zinc from its ores, and during recent years there have been great developments in the processes. The three big producers of electrolytic zinc are, The Anaconda Copper Company of America, The Consolidated Mining and Smelting Company of Canada, and The Electrolytic Zinc Company of Australasia.

The high cost of electric power has operated against all the processes, whilst in many the chief difficulties encountered were due to the deposition of the metal in the form of zinc sponge mixed with zinc oxide, which could not be melted, as it ignited on being heated. The latter difficulties have, however, now been overcome.

" More and more is it evident that the greatest difficulties in the electrolytic process precede the electrolysis itself. Given the right kind of electrolyte, there is no great difficulty in performing the electrolysis; but it may be costly to remove impurities in the hydrometallurgical part of the process in order to obtain the right kind of electrolyte. Also, there may be difficulties in making an adequate extraction of zinc in leaching the ore." ‡

" The most important thing in the metallurgy of zinc in 1915 was the inauguration of electrolytic zinc production direct from ore on a large experimental, even a commercial, scale, at several places, the most important of these being at Anaconda, Mont., where the production of electrolytic spelter at the rate of about 5 tons per day was begun. The results are considered so favourable that the Anaconda Company has commenced the erection at Great Falls, Mont., of a plant capable of producing 35,000 tons of electrolytic spelter per annum." §

The growing production by flotation of a high-grade concentrate, containing from 50 to 55 per cent. of zinc, favours the electrolytic process, because the excessive fineness of this material gives rise to great difficulties in the ordinary distillation process.

There are, however, several serious limitations to the commercial application of the various processes. According to Mr. W. R. Ingalls,|| the chief authority on the metallurgy of zinc, the commercial production of electrolytic zinc is unlikely to be successful, except where the following conditions prevail :—

" (1) Exceptionally cheap hydro-electric power, such as the 6 or 7 dollars

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* *Trans. Inst. Min. and Met.*, 1911, p. 411.

† " Twenty-five Years' Progress of Electrolytic Zinc," O. C. Ralston, *Trans. Am. Electrochem. Soc.*, 1927, li., p. 129.

‡ Ingalls, *Eng. and Min. Journ.*, Jan. 1919.

§ Ingalls, *ibid.*, March, 1916.

|| *Op. cit.*

per annual horse-power of Norway and Sweden, were available; or (2) unless use could be made of the anode reaction, such as the liberation of chlorine by the electrolysis of a chloride solution and the employment of it for some chemical manufacture, as at Winnington, England; or (3) unless certain especially favourable conditions otherwise existed. By the last, I mean such things as high grade of the run-of-mine ore, a kind of ore that will give up a high percentage of zinc by lixiviation with sulphuric acid, an ore high in silver, and possibly lead."

"In the treatment of the Butte ore at Anaconda (see below) about all the favourable conditions that I have enumerated under the third head exist. The ore raised from the mine is of rather high grade; it is of a character that enables 90 per cent. of the zinc, or more to be extracted by sulphuric-acid lixiviation, and as zinc ores go, it is exceptionally high in silver (the concentrated ore going 20 ozs. silver per ton or thereabouts). Moreover, the Anaconda Company is introducing zinc extraction in connection with its other great metallurgical work, thus dividing general and administrative expenses, etc. It is able to obtain moderately cheap power at Great Falls, and finally, what is not least in importance, it possesses about the best metallurgical organisation of any concern in the United States."

*Electrolytic Zinc Process, Anaconda Copper Co., Great Falls, Mont.**—The material treated is a concentrate containing Zn 33 per cent. and Fe 20 per cent. It is roasted in modified Wedge furnaces with powdered coal as fuel. In general, roasting should be done at between 600° and 625° C.

The leaching is continuous and is carried out in two steps:—(1) A neutral leach where all the calcine and about one-half of the total acid is added; (2) an acid leach where no calcine and the remainder of the acid is added. The solution for the neutral leach is made up with one-half of the spent electrolyte and the leach liquor from the acid leach. This mixture is run into the first of a series of seven continuous leaching Pachuca vats containing the charge of calcine.

Calcine is fed into the next three Pachuca vats in such a manner that there is an average drop of 2·5 per cent. acid in each vat. Nothing is added to the fifth vat, which is used as a control vat in which the acid should be nearly, or completely, spent. One-sixth of the total amount of calcine is added to the sixth vat, together with a small amount of limestone. The excess of base contained in the calcine and limestone completely precipitates the ferric iron, the gelatinous silica, and part of the copper. The precipitates, together with the insoluble residue, carry down the arsenic and antimony.

The seventh Pachuca is also a control vat.

The discharge from the last vat goes to classifiers, which remove the sand for re-grinding and further treatment. The overflow from the classifiers flows to Dorr settlers, which discharge a clear liquid for the purification vats, and a spigot product which forms the feed to the acid leach.

The ground sand and the settler spigot product are leached in three Pachuca vats with the remainder of the acid from the electrolytic vats and sent to the acid settlers. The overflow from the vats is maintained at 0·5 per cent. acid.

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* Abstract of Paper by Frederick Laist and F. F. Frick, Anaconda, J. O. Elton, and R. B. Caples, Great Falls (Am. Inst. Min. and Met. Eng. Meeting, Feb., 1921).

The spigot product is filtered by Oliver filters. The filtrate is combined with the acid settler overflow and goes to vats where scrap zinc and scrap iron are added to precipitate most of the copper from the solution. It is then pumped to the first of the neutral leach Pachucas and forms part of the leach added.

The overflow from the Dorr settlers is pumped to twelve Pachuca vats in which it is treated successively with zinc sludge and zinc dust to remove, in two stages, the copper and cadmium. After this precipitation the vats are discharged into settlers, the overflow from which is passed through Shriver clarifying presses.

The clear solution is electrolysed in lead-lined wooden vats containing 27 rolled sheet aluminium cathodes and 28 pure lead anodes, the distance between successive cathodes being 4 inches and between anode and cathode $1\frac{3}{4}$ inches. The best deposits are obtained with a current density of 22 to 24 ampères per square foot, and by the addition every two hours of 1 to 1·5 oz. of glue per ton of metal deposited. The cathodes are stripped every forty-eight hours and produce two sheets of zinc, each weighing from 15 to 20 lbs. The zinc cathode sheets are melted in reverberatory furnaces, ammonium chloride being used as a flux.

The residue from the leaching of the ore is smelted in reverberatories to produce a leady matte containing most of the Cu, Au, and Ag, a fume containing the greater part of the Pb, and a slag with about 11 per cent. Zn, which can be worked up later.

One of the most successful processes is that devised by Höpfner, which was in use with some modifications at the Brunner Mond Alkali Company's Works near Northwich for several years, but has now been given up. The process consists in the electrolysis of a solution of zinc chloride, using carbon anodes and rotating discs of zinc as cathodes, when pure zinc and chlorine which is available for the manufacture of bleaching powder are obtained.

In this process the ore, or burnt pyrites containing zinc, is roasted with sodium chloride, to convert the zinc into chloride, but at the works mentioned the ore is roasted to convert the zinc into oxide, which is then transformed into zinc chloride by CO_2 and a solution of $CaCl_2$, the operation being conducted under pressure (*Prost*).*

$$ZnO + CaCl_2 + CO_2 = ZnCl_2 + CaCO_3.$$

The $CaCl_2$ used is a product of the Solway soda process. The solution of zinc chloride is purified by a series of operations analogous to those devised by Höpfner. The iron and any manganese are precipitated by means of chloride of lime and calcium carbonate, and the other metals, copper, lead, etc., by the addition of zinc fume to the clear solution. The solution of zinc chloride for electrolysis should contain from 0·08 to 0·12 per cent. of free hydrochloric acid.

The anodes are carbon plates placed in special cells fitted with pipes for carrying away the chlorine set free during the process. The chlorine is utilized in the manufacture of chloride of lime, $Ca(OCl)_2$.

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* Prost, *Cours de Metallurgie des Metaux autres que le Fer.* Paris and Liege, 1912, p. 142.

The cathodes are rotating zinc discs, upon which the zinc is deposited in a compact form. Recently it has been proposed to use rotating cylinders instead, with a view to increased compactness.

The intensity of the current is 100 ampères for 10·8 square feet, with an E.M.F. of 3·3 to 3·8 volts. The spelter is very pure, containing only 0·01 per cent. of iron.

Electric Smelting of Zinc Ores.—The chief drawbacks that impede the commercial success of the application of the electric furnaces to the smelting of zinc ores are the cost of the current and of the electrodes, the loss of metals, and the difficulty of obtaining a fair proportion of the zinc as metal and not as oxide, which has to be re-treated.

The most notable and important works are situated in Norway and Sweden, where electricity is generated by water power at a low cost.

Of the several methods which have been devised, that carried on at Troilhätten, in Sweden, may be selected as typical, and is of special interest from the important work which has been conducted there by Mr. F. W. Harbord. During the smelting campaign, which he carried out under strictly working conditions, 537 metric tons of ore were smelted. Seven furnaces were employed for 27½ days, and the ore consisted of 518 tons of roasted Broken Hill slime (containing 32 per cent. zinc, 23 per cent. lead, and 25 ozs. silver per ton), 19 tons of calamine, and 22½ tons of zinc-lead powder previously produced.

The yield was 160·8 tons of crude zinc and 36 tons of powder. The crude metal averaged about 79 per cent. zinc, 20 per cent. lead, and 0·6 per cent. iron. The lead tapped with the slag was remelted and yielded 41 tons of marketable lead, containing 141 ozs. of silver per ton. There was also obtained 17 tons of lead which had leaked from the furnace, assaying 21 ozs. of silver per ton. The total recovery of the metals was 64 per cent. of the zinc, 74 per cent. of the lead, and 46 per cent. of silver, exclusive of those in the powder. Mr. Harbord attributes the unduly large losses of lead and silver to the retention of some of these metals in the walls and hearths of the furnaces. The consumption of electric current averaged 2,078 kilowatt-hours per ton of ore smelted.

The furnaces are of the resistance type, with one large vertical carbon electrode passing through the roof, the other electrode being a carbon block in the bottom of the furnace.

Each furnace has a capacity of about 3 metric tons, and smelts about 2·8 tons of ore in twenty-four hours. The roasted ore mixed with anthracite or coke and flux is charged into the furnace, where most of the zinc and some of the lead are volatilized, and condense chiefly as crude spelter high in lead, and partly as blue powder or fume, which has to be re-treated. The other part of the lead is reduced to metal and is tapped out with the slag. It contains a considerable proportion of the silver. Some matte is formed, and this and the slag contain some of the lead, zinc, and silver.

As regards the success of the process, Mr. Harbord points out that its weak point is the large amount of metallic powder produced in proportion to the metals He says further in his report, "the recovery of a large percentage of metals as metals is admittedly a very difficult problem, but that the present practice can be very greatly improved upon, I have not the least doubt, leading to decreased consumption of energy and reduction of labour costs."

The process used is intended for the treatment of complex zinc-lead sulphide ores, such as intimate mixtures of blende, galena, copper, and iron pyrites, which are of extensive occurrence, but of little commercial value, and more particularly Broken Hill slime.

At Trollhätten many thousand tons of zinc have been made since Mr. Harbord's smelting campaign.

According to Professor Stansfield,* "The electric furnace process holds out the hope that roasting can be dispensed with, or at least that it need not be nearly so thorough. This possibility depends on the removal of the sulphur in the electric furnace in combination with metallic iron, or more cheaply with calcium supplied in the form of lime. O. H. Brown and W. F. Oesterle have studied the latter reaction, and find that it takes place very completely, in the electric furnace, according to the equation—

$$ZnS + CaO + C = Zn + CaS + CO."$$

He also says, "While recognizing the serious difficulties which stand in the way of a successful commercial use of the electric furnace for smelting zinc and zinc-lead ore, he still believes that this will in time be accomplished, and that in favourable localities a large industry will be built up on the electric smelting of zinc."

A process for smelting complex zinc ores is also being carried on, on a small scale, by Cote and Pierron near Pau (France), in which zinc sulphide is decomposed by metallic iron in an electric furnace. The process is based on the fact that iron replaces lead in lead sulphide at a comparatively low temperature, and zinc in zinc sulphide when the temperature is increased. It is claimed for the process that by its means zinc and lead can be completely separated.

The furnace is circular, with sides and bottom lined with graphite, the top being a low dome of fire-brick. A carbon electrode, which can be raised or lowered, passes through an opening in the centre of the top, the other electrode, a cone of graphite, projects from the hearth. The furnace is charged through the roof, and the lead, slag, and iron sulphide are tapped through an aperture in the side. The volatilized zinc passes through an outlet in the upper part of the furnace to the condenser, which consists of a cylindrical shaft-like chamber of fire-brick filled with coke or anthracite, and provided with a taphole at its base for the discharge of the condensed zinc.

The charge consists of a mixture of blende, iron, and lime. After the furnace has been heated by lowering the electrode to produce a short arc, the charge is introduced, and the first reaction of iron on lead sulphide is effected at a relatively low temperature. The resulting lead is then tapped. The electrode is now raised, the temperature increased by arc and resistance, and the decomposition of the zinc sulphide by the iron brought about. The zinc distils over, and is condensed in the condenser, the carbon in which is kept at a red heat, to diminish, as far as possible, the formation of zinc fume. Finally, the iron sulphide and the slag are run out.

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* Stansfield, *Journ. Inst. of Metals*, 1916, vol. xv., pp. 291 and 292.

CADMIUM.

Physical Properties.—Cadmium is a white metal with a bluish tinge and brilliant lustre, and in many of its physical properties it is closely allied to zinc. In hardness it is intermediate between tin and zinc. It is malleable and ductile, and can be beaten out into thin foil and drawn into wire. When bent it " cries " like tin.

Its specific gravity when cast is 8·60. The melting point of cadmium is 320° C., and its boiling point is 778·6° C. (*Becquerel*), that of zinc being about 915° C. Hence it can be separated from zinc by volatilization.

The atomic weight of cadmium is 112·4.

Chemical Properties.—At ordinary temperatures cadmium is scarcely altered in dry air, but when heated to redness it burns readily, evolving brown fumes of the oxide. Nitric acid is the best solvent of cadmium, but the metal is also soluble in hydrochloric and sulphuric acids, and in solutions of the alkaline hydroxides.

It is precipitated from its saline solutions by zinc, hence the purification of zinc sulphate solutions by means of zinc powder, in preparing them for electrolysis and in the manufacture of lithopone, is now a source of cadmium.

Cadmium oxide, CdO, is of a brown colour, infusible, but soluble in acids and in ammonia. It is reduced to metal by carbon and carbon monoxide in the same way as zinc oxide, but at a lower temperature. Cadmium also volatilizes at a lower temperature than zinc. In consequence of these differences, the metals can be separated in a dry way, and on them the operations for the commercial production of cadmium are based.

Cadmium Sulphide, CdS.—This sulphide occurs in nature as the mineral Greenockite in Scotland and Bohemia, but in such very small quantities that it is of no commercial importance as a source of cadmium. It is prepared as a brilliant yellow pigment, cadmium yellow, for the use of artists, by precipitating a solution of a cadmium salt. The colour of the pigment has various shades of yellow, according to the strength, acidity, temperature, and other conditions prevailing when H_2S is passed into the solution.

It is also and chiefly used to give colour and lustre to glass and porcelain (*Siebenthal*).

Alloys and Uses.—Silesian cadmium generally contains 99·5 to 99·75 per cent. Cd. Cadmium alloys with a number of metals, and forms an amalgam with mercury which is used in the cadmium standard (Weston normal) cell. As the alloys of silver and cadmium are softer, whiter, and more malleable and ductile than the silver and copper alloys, cadmium is somewhat extensively employed, especially in America, as a constituent of sterling silver for silver wares. The alloys rich in silver are perfectly homogeneous; this was first pointed out by Kirke Rose, of the Royal Mint, who for that reason suggested their use for the preparation of trial plates for assay purposes.

When cadmium is added to lead-tin-bismuth alloys it lowers their melting points to a remarkable extent. Thus an alloy of bismuth 2 parts, tin 1 part, and lead 1 part, which melts at 93·75° C., has its melting point lowered to 75° C. by the addition of 8 to 10 per cent. of cadmium, whilst an alloy composed of cadmium 14·3, tin 19·0, lead 33·1, and bismuth 33·6 parts has the very low melting point 66° C. In consequence of this property, it enters into the composition of all the so-called "fusible alloys," which are used for safety plugs, clichés, and soft solders.

During the war, owing to the necessity for the conservation of tin, cadmium was largely used as a substitute for part, or the whole, of the tin in the manufacture of solder.

Upper Silesia was the chief producer of cadmium; some is also produced in Great Britain, and 64 metric tons in the United States in 1918. The consumption of the metal, however, is but small, its chief uses being for the manufacture of silver ware, the preparation of alloys, and in electroplating. A small but insignificant quantity is consumed in the preparation of cadmium sulphide as an artist's pigment.

Sources of Cadmium.—There is no ore of cadmium in the usual acceptation of the term, as the mineral Greenockite, cadmium sulphide, is of too rare and limited occurrence to be regarded as such. The metal is, however, found in many zinc ores, blende, and calamine, and although only present in very small quantities, yet the cadmium of commerce is practically entirely obtained from them. The amount of cadmium contained in zinc ores from different localities has been the subject of a painstaking examination by E. Jensch,* in which he found that scarcely any ores contained more than 0·45 per cent. of the metal. The maximum content of the ores in Upper Silesia, formerly the chief producer of cadmium, was only 0·306, and the average 0·102 per cent. In blende from Matlock and Lanarkshire over 0·4 per cent. was present. According to W. G. Waring, the average content of cadmium in thirty shipments of blende from Joplin, U.S.A., in 1904, was 0·36 per cent.†

The chief sources of cadmium are the electrolytic zinc plants of the United States, Australia and Germany. It is also obtained from zinc fume (blue powder) from the distillation, and the flue dust from the roasting, of zinc ores.

Another important source is the bag-house fumes from lead and copper smelting plants. These fumes gradually become enriched in cadmium until in some bag-houses they may reach 8 to 15 per cent.

Extraction of Cadmium—(1) *By Distillation.*—As has already been pointed out, the operations, which consist of a series of fractional distillations, are based on the fact that cadmium oxide is reduced by carbon and carbon monoxide at a lower temperature than zinc.

In the ordinary distillation of zinc ores, the cadmium hence is first reduced and volatilized, and will be chiefly found in the blue powder, which collects in the condensers and prolongs during the first two hours. This is collected, and may contain from 5 to 8 per cent. of cadmium. The zinc dust subsequently collected will not contain more than 1·2 to 2·0 per cent. In the flue dust from the roasting of the ores rarely more and generally less than 2·00 per cent. of cadmium will be found. These cadmium-bearing materials, after having been mixed with ground coke, are charged into either Belgian or muffle-shaped retorts, to which conical condensers of sheet iron about 5 feet long and tapering to about 2 inches are attached. The temperature of the muffle during distillation is kept low, about 800° C., so that, as far as possible, only the cadmium oxide will be reduced. The product obtained in the condensers will be chiefly in the form of powder. It is then again distilled in a similar manner, but usually in a somewhat smaller retort. At some works cast-iron retorts are employed for the redistillation.

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* *Berg. und hüttenmannische Zeit.*, 1899, p. 189.

† Ingalls, *Min. Ind.*, 1905, p. 590.

The metallic cadmium collects in the sheet-iron condenser in a solid state. It is scraped out, melted under tallow, and cast into small sticks, 8 to 12 inches long and $\frac{1}{4}$ inch in diameter. The residue from the retorts is returned to the spelter works.

(2) *By Wet Methods.*—(*a*) The flue dust or bag-house fume is treated in Colorado by mixing with strong sulphuric acid, then made into a paste with water and heated until a cake is formed, which is crushed and heated to 325° C. in an iron pan. The resulting powder is leached with dilute cadmium sulphate solution at 65° C. The clear solution is siphoned into purification vats, in which arsenic and copper are precipitated. The purified solution is heated for several days in lead-lined wooden tanks containing suspended slabs of zinc. The precipitated spongy cadmium is compressed into cylinders, cut into pieces and distilled from graphite retorts. The metallic cadmium is then melted in a kettle and cast into sticks.

(*b*) The precipitate from electrolytic zinc plants, containing copper, cadmium and zinc, is roasted and then digested with dilute sulphuric acid. Practically the whole of the copper remains in the residue and the solution containing cadmium and zinc is treated with "blue powder" in an agitation vat in the absence of air. Most of the zinc remains in solution. The precipitate, containing cadmium and a little zinc, is roasted and treated with dilute sulphuric acid. The solution, after being freed from any copper that may remain in it, is electrolysed in cells having revolving aluminium disc cathodes. Any cadmium remaining in the filtrate is recovered by precipitation with zinc dust. The cathodes are melted under a high flash-point oil and poured into ingots.

TIN.

Physical Properties.—Tin is one of the whitest of metals, almost as white as silver, but with a very faint yellowish tinge.

It has a brilliant lustre, which is diminished by the presence of lead, arsenic, antimony, iron, bismuth, and other foreign metals.

The structure of tin is distinctly crystalline. If its surface be brushed over with warm dilute sulphuric acid containing nitric acid, or with hydrochloric acid containing free chlorine, it becomes covered with a network of crystals exhibiting the appearance which has been termed *moiré metallique.*

When a bar is bent it emits a peculiar crackling sound, called the "cry" of tin. This is due to the crystals grinding against one another.

Malleability and Ductility.—Tin is very malleable and ductile, harder than lead, but softer than gold. It can be hammered and rolled at ordinary temperatures into sheets of extreme thinness, as, for example, tinfoil. It is necessary, however, that slabs or castings intended for rolling should not be cast at too high or too low a temperature, or they will be more or less brittle.

At 200° C. it can be powdered.

Tenacity.—Its tenacity is low, rather less than 1 ton per square inch.

Specific Gravity.—The specific gravity of pure tin when cast is 7·29, whilst that of commercial tin sometimes reaches 7·5, owing to the impurities usually present having a higher specific gravity than it.

Action of Heat.—Tin melts at 232° C. It boils at about 2,100° C., but is said to be perceptibly volatile at about 1,200° C.

When tin is exposed to severe cold its molecular structure undergoes a complete change, its volume is increased, and it breaks up into a grey granular powder. This is due to the production of an allotropic modification (grey tin) of the ordinary metal (white tin).

According to Cohen, the change may begin at 64° F., reaching its maximum at − 40° F. This is of considerable importance as regards the storage of tin and tin articles in countries where the temperature is liable to be extremely low. One well-known case of this change on a large scale occurred in a consignment of Straits tin, stored in a Custom house in Russia during the winter of 1868, which was found to be in the state of powder when it had to be removed.

Electrical Conductivity.—Its electrical conductivity is 11·3, that of silver being taken at 100·0.

Atomic Weight.—The atomic weight of tin is 119·0.

Chemical Properties.—Tin is not acted on by air or water at ordinary temperatures, but if heated in the air above its melting point it becomes covered with a greyish layer, consisting of stannic oxide (SnO_2) and tin. Tin is readily soluble in hot hydrochloric and in boiling sulphuric acids; in the latter case SO_2 is given off and stannic sulphate formed. Cold sulphuric acid has but little action on the metal.

Nitric acid (sp. gr., 1·3) oxidizes it to metastannic acid ($H_{10}Sn_5O_{15}$), which is insoluble in excess of the acid.

Aqua regia dissolves the metal forming stannic chloride.

Tin is soluble also in hot solutions of sodium and potassium hydroxides, stannates being formed.

Tin Oxides.—Of the two oxides, SnO and SnO_2, the latter, stannic oxide, is the most important. It occurs in nature as cassiterite or tinstone, the chief source of the metal.

When tin is heated to a high temperature in the air SnO_2 is the oxide which is formed. It is white or straw yellow in colour, insoluble in acids, but soluble in solutions of the alkalies. When heated with carbon, carbon monoxide, hydrogen, or potassium cyanide, it is reduced to metal. It combines with alkalies in the dry way, and if the alkali be in sufficient quantity soluble stannates are formed.

Tin Sulphides.—Stannous sulphide (SnS) and stannic sulphide (SnS_2).

If stannous sulphide is roasted in the air SO_2 is given off and SnO_2 is formed. It combines with or is dissolved by other sulphides, and hence may be found in mattes.

Commercial Tin.—The impurities generally present in the tin of commerce are copper, arsenic, antimony, lead, iron, bismuth, and traces of sulphur and silver; tungsten, manganese, and stannic oxide are sometimes also found. In the following table, issued by the London Metal Exchange, are given analyses of some of the most important brands of tin.

From this table it will be seen how very pure are certain brands of the commercial metal, Billiton tin containing 99·96, Cornish tin (Williams, Harvey & Co., No. 4) 99·94, and several others over 99·90 per cent. of tin, a degree of purity rarely found even in refined gold. According to the recent action of the London Metal Exchange, tin over 99·75 per cent. will be held to be the standard as regards quotations of the price of the metal. Banca, Straits, and Australian tin, however, command a premium over the price for standard. The purer brands are chiefly in demand for the tin-plate manufacture, as the presence of impurities tends to prevent a bright and perfect coating from being obtained. The less pure brands, however, find buyers among the makers of alloys in which impurities have less detrimental effects. The tendency of all the impurities given in the above table is to increase the hardness and diminish the malleability of the metal.

If tin is melted at a low temperature and poured into an open stone mould it should present a perfectly resplendent surface. If the surface has a frosted appearance the tin is impure, and the frosting is proportional to the impurities.

Uses of Tin.—Tin is extensively employed for the manufacture of tin plate, which was thin sheet iron, now mild steel, coated with the metal, and also largely for the manufacture of the alloys mentioned below.

Alloys of Tin.—Tin forms alloys with many metals, those with copper being of special industrial importance (see p. 63). It alloys with lead in all proportions, and all the alloys are malleable and ductile. The eutectic contains 37 per cent. of lead, and melts at 180° C.

The tin-lead alloys are largely used as solders.

Analyses of Commercial Brands of Tin.

	Tin.	Antimony.	Arsenic.	Lead.	Bismuth.	Copper.	Iron.	Silver.	Sulphur.
Banca,	99·950	0·007	nil	trace	nil	0·018	0·045	nil	trace
Billiton,	99·960	0·006	nil	nil	nil	0·023	nil	nil	nil
Penang,	99·939	trace	0·003	trace	nil	0·016	0·028	nil	0·004
Singapore,	99·870	0·008	0·045	0·034	0·003	0·052	0·003	0·006	0·005
Mt. Bischoff,	99·795	0·015	0·063	0·037	0·005	0·035	0·042	trace	0·008
Pyrmont.	99·938	0·017	0·019	trace	nil	0·022	trace	nil	0·004
Irvine Bank,	99·580	0·062	0·034	0·221	0·025	0·126	0·002	0·018	0·004
Williams, Harvey & Co., No. 1*a*,	99·860	0·015	0·040	0·004	0·005	0·047	0·003	nil	0·006
Williams, Harvey & Co., No. 2,	99·560	0·166	0·037	0·162	0·007	0·050	0·005	trace	0·013
Williams, Harvey & Co., No. 2,	99·350	0·245	0·065	0·223	0·015	0·042	0·016	trace	0·013
Williams, Harvey & Co., No. 3,	99·200	0·300	0·037	0·396	0·007	0·100	0·013	0·014	0·006
Williams, Harvey & Co., No. 4,	99·941	0·011	0·022	trace	0·001	0·020	trace	trace	0·005
Penpoll, No. 1.	99·720	0·118	0·054	0·041	0·007	0·052	0·004	0·009	0·007
Penpoll, No. 2,	98·710	0·569	0·042	0·546	0·055	0·103	0·007	0·015	0·004
Penpoll, No. 3,	99·300	0·325	0·056	0·212	0·050	0·088	0·002	0·021	0·009
Redruth.*	99·160	0·176	0·053	0·177	0·017	0·445	0·014	0·006	0·008
Th. Goldschmidt, No. 1,	99·860	0·004	nil	0·102	nil	0·043	trace	nil	trace
Th. Goldschmidt, No. 2,	99·460	0·015	nil	0·425	nil	0·069	trace	nil	trace
Th. Goldschmidt, No. 3,	99·150	0·122	0·046	0·143	0·112	0·352	0·007	0·006	trace
Chinese, No. 1,	99·343	0·031	0·040	0·434	0·007	0·052	0·010	trace	0·011
Wing Hong & Co., No. 2,	98·662	0·039	0·035	1·035	0·012	0·134	0·014	trace	0·011
Wing Hong & Co., No. 3,	95·280	0·381	0·050	3·995	0·020	0·106	0·026	0·018	0·008

* Cobalt, 0·012 per cent.

The following being those commonly employed :—

	Tin.	Lead.	
Solder for electric fittings,	94·5	5·5	Hughes.
Tinsmith's solder,	60 66·6	40 33·3	
Plumber's solder,	50 33·3	50 66·6	

An important alloy is that commonly known as pewter. It consists of 80 per cent. of tin and 20 per cent. of lead, and if used for the manufacture of drinking or domestic vessels the lead must not exceed that percentage, to avoid risk of lead poisoning. In France the proportion of lead in pewter for these purposes is limited by law to 18 per cent.

Pewter is also made by the addition of a small percentage of copper to tin. This gives a metal which is harder but not of such a good colour as the above. Two old spoons of this alloy, of the sixteenth century, analysed in the author's laboratory, had the following compositions :—

Sn,	97·00	95·60
Cu,	1·42	1·06
Pb,	1·65	3·64

Tin also alloys readily with antimony, but simple alloys of the two metals are very little employed. On the other hand, triple alloys of tin and antimony with lead, copper, and other metals are in very extensive industrial use.

The most important, and by far the most extensively used, of these alloys are the "white metals," the so-called "antifriction alloys," which are employed for the lining of bearings, axle boxes, etc., of engines and machinery. In structure these alloys consist of small hard particles embedded in a plastic matrix; the former tends to resist wear, and the latter enables the metal to adapt itself to any imperfections of adjustment, hence it is that they diminish friction and prevent overheating.

These alloys vary greatly in composition, and necessarily so, as an alloy suitable for heavy slow-running engines would, it is obvious, be quite unfit for light high-speed machinery.

Typical examples of the composition of antifriction metals are given in the following table :—

ANTIFRICTION METALS.

	Sn.	Sb.	Cu.	Pb.	Authority.
Babbitts' metal, normal,	90·0	7·0	3·0	..	Sperry.
,, hard,	88·0	4·0	8·0	..	,,
,, soft,	84·0	7·4	3·0	5·6	,,
German Railroads' specification,	83·3	11·1	5·6	..	
Swiss Railroads,	80·0	10·0	10·0	..	Thurston.
Axle bearings for pinions for motors—Electric Railways,	82·0	14·0	4·0	..	Hughes.

Another class of alloys, known under the name of Britannia metal, consists of variable proportions of tin and antimony with small quantities of other metals. They are silvery-white alloys with a slight bluish tinge, take a high polish, and are in extensive use for the manufacture of tea pots, coffee pots, and other vessels and articles for domestic use.

The effect of antimony is to give hardness and brilliancy to the metal, whilst copper, although it also produces hardness, has an injurious effect upon the colour unless present in very small amounts. The compositions of a few characteristic examples of Britannia metal are as follows :—

	Sn.	Sb.	Cu.	Zn.
Britannia metal (English) for spinning,	94·0	5·0	1·0	..
,, sheet, . . .	90·6	7·8	1·5	..
,, for casting, . .	90·6	9·2	0·2	..
Queen's metal, . .	88·5	7·1	3·5	0·9

Tin and arsenic unite in all proportions. When 6 per cent. of arsenic is present the alloy has a largely crystalline fracture, and might be mistaken for bismuth if it had the right tint of colour. Tin and iron also have a great affinity for each other, thus in tin plate at the junction of the iron or mild steel with the tin coating a true alloy is formed.

When an alloy of tin and iron with an excess of tin is cautiously heated, tin will liquate out, and a less fusible alloy of tin and iron will remain. The residual alloy will generally consist approximately of 35 per cent. of tin and 65 per cent. of iron. This fact is important, as on it is based the separation of iron from crude tin in the refining process, the residual alloy then being called "hardhead."

There are no alloys of tin and iron, or of tin and arsenic, of any value.

Ores of Tin.—The oxide SnO_2, which occurs in nature as the mineral cassiterite, tinstone, or black tin, is the only ore of tin ; the mineral stannite, called also tin pyrites and bell-metal ore, a tin sulphide, containing about 25 to 28 per cent. of tin, intimately associated with copper, iron, and zinc sulphides in varying proportions, being of too rare occurrence to be considered an ore.

Cassiterite when pure contains 78·6 per cent. of tin. Its specific gravity is high, ranging from 6·3 to 7·1. Its colour varies from brown to black. The term black tin is applied to the concentrate obtained by dressing the ore. It contains on an average 65 to 70 per cent. of tin. Cassiterite occurs in veins or lodes and stockworks, when it is called "lode" tin, and in alluvial sands and gravels as "stream" tin. When it presents a fibrous structure it is called "wood" tin. The lodes are usually in granite, clay-slate, and mica schists, in which the mineral may be associated with copper and iron pyrites, wolfram, mispickel, galena, molybdenite, bismuth glance, magnetite, ilmenite, fluorspar, etc.

In the alluvial deposits stream tin occurs as water-worn nodules and grains of tinstone in association with but few metallic minerals. It is obvious, therefore, that lode tin will, as a rule, yield a less pure metal than stream tin.

Stream tin, however, forms almost the entire production of the Malay Peninsula, of Banca and Billiton, and is, in fact, by far the most important source of tin in the world.

The ore as mined in Cornwall is very variable in its content of cassiterite, and on account of the wide range in the market value of the metal from time to time, and the varied conditions prevailing at different mines, no definite rule can be laid down as to the tenor of the mineral required for payable ore. With only 20 lbs. of black tin per ton some mines have failed to pay a dividend.

In the Malay States the average content of the deposits worked ranges from 11 to 18 lbs. cassiterite per ton or less than 1·0 per cent., but it is said that a little over 1 lb. per ton of gravel will yield a profit.

In Tasmania, at the Anchor Mine at Lottah, where a granite stockwork is being worked, the ore is of very low grade, said to be 3½ lbs. of black tin per ton of ore crushed.

The principal producers of tin ore, arranged in the order of their importance, are the Malay Peninsula, especially the provinces of Perak and Selangor; Bolivia; the Dutch Islands of Banca and Billiton; Nigeria; China; Siam; Burma.

Others of lesser prominence are Africa (in the Transvaal, S.W. Africa, East Africa, and the Belgian Congo), Australia, Cornwall, Japan and Portugal. The alluvial deposits of Northern Nigeria now yield considerable quantities of tin.

On the other hand, the principal producers of metallic tin are the Malay Peninsula, England, Banca, Germany, Australia, Billiton, and China. Very little metallic tin is produced in Bolivia, the ore is all exported in the form of a concentrate termed "barilla," with an average content of about 60 per cent. tin.

The Extraction of Tin.—The extraction of tin from its ores is practically always carried out by dry methods, wet or electrolytic methods being confined to the extraction of the metal from tin-plate scrap.

Concentration.—The ores are almost invariably too poor to be treated directly, and must hence first be concentrated; they are, too, generally contaminated with metallic and other minerals, which it is necessary to remove, as far as possible, before they can be smelted. Further, as the smelting of the ore has to be performed with the production of a minimum quantity of slag, it must not contain too much lime or silica. The ore is prepared partly by hand picking, but chiefly by a series of mechanical processes, in which advantage is taken of the high specific gravity of cassiterite.* These "dressing" processes are often accompanied by roasting, to decompose sulphides and arsenides, and sometimes by chemical treatment, to dissolve out part of the metallic oxides formed.

In the Malay Peninsula, where the ore is chiefly in the form of stream tin, the concentration is effected by hand picking, and a series of washing processes in sluices and on tables. In Malayan dredging practice jigs have come into common use. The partially concentrated tin ore resulting from the jig treatment is taken ashore from the dredge and washed by native labour to produce a high grade concentrate. But, when the ore is obtained from lodes, as in Cornwall and elsewhere, it is in lump form, and has to be crushed, stamps and rolls being generally employed, after which it is submitted to an elaborate system of washing operations. By these measures the lighter minerals are separated and the tin content of the ore raised to 50 per cent., or even 70 per cent., if sulphides and arsenides are not present in large amounts.

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* For details of Cornish practice see *Trans. Inst. Min. and Met.*, 1928, vol. xxxvii., pp. 73 and 78.

In Cornwall, the usual practice consists in the use of concentrating tables for coarse sand, frue vanners for the finer or middling products, and round frames for the slimes.

As the ore, however, is often contaminated with iron, copper, and arsenical pyrites, and occasionally with wolfram, simple mechanical dressing operations by means of water are insufficient for the removal of these impurities. For the removal of the sulphur and arsenic roasting is necessary, the ore having been first concentrated to about 25 per cent. The operation is carried out in simple hand-worked reverberatory furnaces, or in furnaces with revolving beds, or in revolving cylinders with continuous discharge. In Cornwall the calciners are worked at a temperature of 600° to 700° C. and consume about $2\frac{1}{2}$ cwts. of coal per ton of concentrate roasted.

The changes which occur in the operation of roasting are as follows: —

The sulphur is oxidized and SO_2 is given off. The arsenic also is oxidized, and the greater part volatilized as As_4O_6 (white arsenic), some remaining as arsenate in combination with the iron oxide or other bases present. When the ore contains much arsenical pyrites the As_4O_6 is condensed and collected in long flues and in condensing chambers.

The copper and iron of the pyrites are oxidized, and copper and ferric oxides are formed, with some copper sulphate and ferric sulphate if the temperature has been low. It has been proposed to roast highly pyritic ores in such a manner that copper and iron sulphates which could be leached out should be produced, but although this is occasionally carried out, there are practical difficulties which prevent more than a portion of these metals from being converted into sulphates, and the leaching is hence imperfect.

A small portion of the SnO_2 is said to be converted into sulphate, otherwise it is unaltered.

Wolfram undergoes no change.

The roasted product is then further concentrated by washing on tables or other dressing appliances, and the ferric oxide, etc., removed.

When copper and bismuth are present in sufficient amounts the roasted ore is further treated with dilute sulphuric or hydrochloric acids, which dissolve the oxides of these metals, but have no action on the cassiterite; they can thus be recovered.

The separation of wolfram is more difficult. On account of its high specific gravity and insolubility in acids it cannot be removed by the treatment just described, yet if left in the ore wolfram gives rise to loss of tin in the operation of smelting, by diminishing the fluidity of the slag, and thus preventing the separation of the metal from it.

At some works the ore containing much wolfram was fused with sodium carbonate in a reverberatory furnace, when sodium tungstate was formed and removed by lixiviation with water. The process, however, was given up as there was an insufficient demand for the salt, and a loss of tin owing to the formation of sodium stannate; the operation, too, entailed considerable expense.

At present as much of the wolfram as possible is separated by hand picking from the ores as mined, and the remainder from the specially roasted concentrate by Wetherill magnetic separators,* after treatment with dilute sulphuric acid.

The operations for the extraction of tin from the concentrate, black tin, resulting from the dressing processes, are :—

1. Smelting for crude tin.
2. Refining the crude tin.
3. Smelting the slags and residues.

Smelting.—The extraction of tin from the black tin concentrate by smelting depends on the reduction of SnO_2 by carbon and carbon monoxide. The temperature required for the reduction is, however, very high (1,000° to 1,100° C.) compared with the melting point of the metal (232° C.), hence when the ore contains iron and other metals they are reduced and alloyed with the tin. As SnO_2 can act either as a base or as an acid, if SiO_2 is present some of the SnO_2 will combine with it, forming a difficultly fusible silicate, whilst if the ore contains excess of lime a calcium stannate may be formed, resulting in either case in loss of tin in the slag. Fluorspar, lime, etc., are sometimes employed as fluxes, but they should be used sparingly, only sufficient being added to give the necessary fluidity to the slag, as the total amount of slag must be kept as low as possible, on account of the tin which it always contains.

One of the first principles in tin smelting is, in fact, to arrange the composition of the charge so that as little slag as is practicable shall be produced; of course, sufficient must be present to protect the reduced tin from oxidation.

Tin smelting is always conducted in England, in the chief smelting works in the Malay Peninsula, in Tasmania, and generally in Europe, in reverberatory furnaces, blast furnaces being employed only for the treatment of slags and residues.

At Banca and Billiton, however, where the ore is rich and pure, blast furnaces are employed, using charcoal as fuel, and producing extremely pure tin. Small blast furnaces of primitive construction are also in use by Chinese in the Malay Peninsula.

The reverberatory furnace has several advantages over the blast furnace in tin smelting, among which the following are noteworthy :—

1. Ore of extreme fineness can be treated. This is important, as tin ore is usually in very fine grains, owing to the treatment to which it has been subjected during concentration.

2. Common coal can be used as fuel, also producer gas and petroleum.

3. The tin is purer, as the reduction of the foreign oxides is less complete, owing to the lower temperature.

4. There is less loss by volatilization for the same reason.

On the other hand, there are the following disadvantages :—

1. The bed of the furnace retains a large quantity of tin, which is only recovered when the smelting campaign is ended.

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* See *Trans. Inst. Min. and Met.*, vol. xv., pp. 2-28. Paper by F. Dietzcsh, "Treatment of Tin-Wolfram-Copper Ores."

2. The slags are richer in tin than blast-furnace slags.
3. The process is intermittent.

The ore treated is the concentrate, black tin, which has been prepared for the smelting operations, as already described. It contains usually about 65 to 70 per cent. of tin, associated with varying amounts of metallic oxides, and usually with silica.

Certain kinds of Bolivian ores are more impure, containing copper, lead, antimony, etc., and only 40 to 50 per cent. of tin.

The furances employed vary considerably in dimensions, and in a few details, which by some smelters are held to be important, but all are closely allied as regards the chief features of their design, and are constructed on the same principles.

Within recent years tin smelting practice has become modernised. This applies to European as well as to Eastern practice. The reverberatory furnace still maintains its supremacy, but has increased considerably in size, and furnaces of 25 to 30 tons of ore capacity per charge are now in use. Coal firing has largely given way to producer gas or oil firing, and this advance has brought with it the use of regenerator chambers for preheating the air required for combustion of the fuel. Regenerator chambers are built either under or above ground at the furnace ends.

A factor that has contributed largely to the modernising of tin smelting practice has been the introduction of the Lodge-Cottrell system of fume collection. The greatest difficulty of the tin smelter in the past has been the loss of tin by volatilisation during smelting operations. The Lodge-Cottrell process has practically eliminated this loss, or at least reduced it to very small limits, and in consequence the tin smelter is now able to smelt at a higher temperature and drive his furnaces faster than formerly.

Tin Smelting at Pulo Brani, Malay Peninsula.—The furnaces in use at

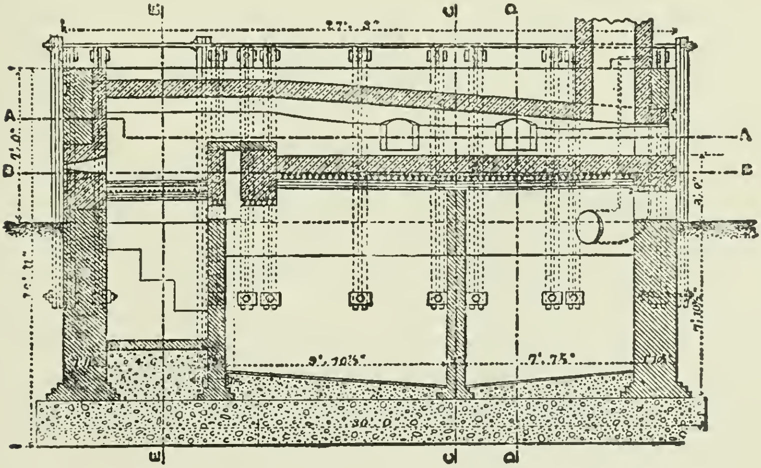

Fig. 200.—Tin Smelting Furnace at Pulo Brani—Longitudinal Section.

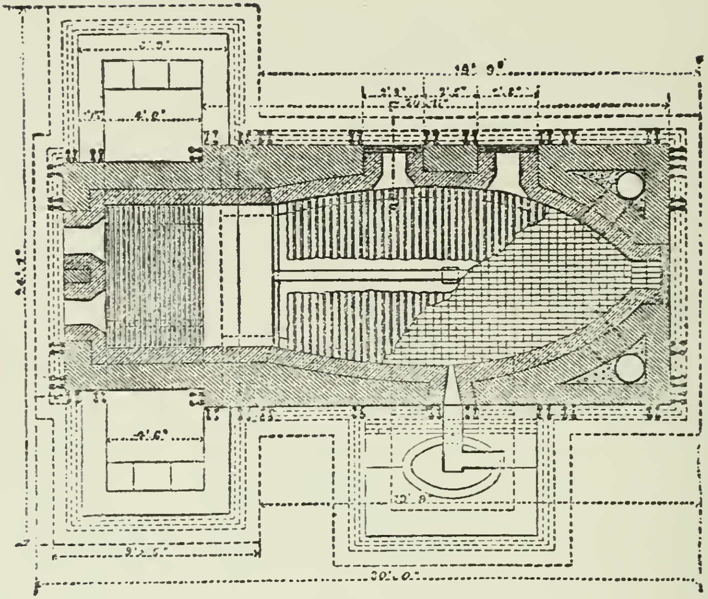
19' 9"
4' 6"
4' 6"
30' 0"

Fig. 201.—Tin Smelting Furnace at Pulo Brani—Section at AA and BB.

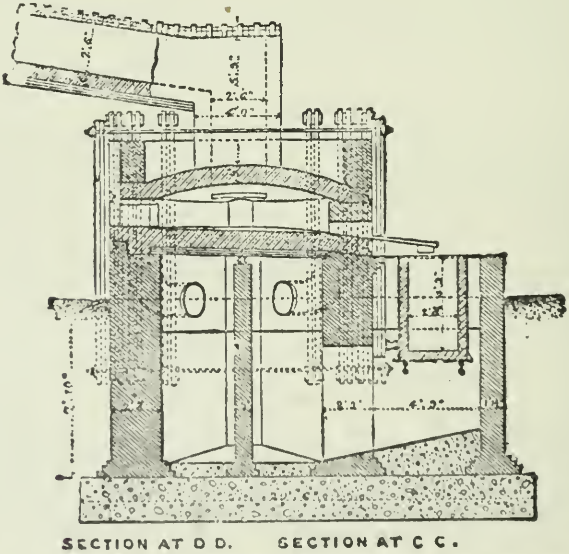
2' 6"
2' 6"
SECTION AT D D.
SECTION AT C C.

Fig. 202.—Tin Smelting Furnace at Pulo Brani.

the works of the Straits Trading Company, in the island of Pulo Brani, near Singapore, the largest tin smelting works in the world, and the scheme of treatment followed there, are typical of the best modern practice. The following description refers to the practice as carried out some years ago, and although the plant has been considerably altered, the details given are still of interest. One of the furnaces is represented in vertical and horizontal sections in Figs. 200, 201 and 202.* An important feature in its construction is that the roof, bed, and lining of the sides can each be removed and renewed independently of one another, and also of the outer walls.

The bed is constructed of fire-brick set on end, and slopes towards the taphole. Its dimensions are—length, 16 feet; breadth at middle, 5 feet 9 inches, and at the fire-bridge, 6 feet.

Below the bed is a cistern of water about 8 feet deep, into which any tin that leaks through falls and is granulated. Any steam generated passes away through two 8-inch tubes near the flue end of the furnace. The fire-bridge, which is hollow, rises 8 inches above the bed, and 2 feet 6 inches above the fire-bars. The dimensions of the fire-place range from 4 feet by 6 feet to 4 feet 6 inches by 6 feet 9 inches, according to the quality of the coal used. There are two fire-doors in the back wall just below the roof for feeding in the fuel. The smelting charge is introduced through two doors in one of the sides of the furnace, and is worked through the door in the front.

The taphole is on the side of the furnace opposite the charging doors, and immediately in front of the taphole an iron vessel with a refractory lining, called by tin smelters a "float," is fixed for the reception of the reduced tin.

The scheme of smelting consists of three operations, not including refining:—

1. Ore smelting, producing ore metal and rich slag.
2. Smelting the rich slag, producing rough metal and poor slag.
3. Smelting the poor slag, producing a more impure metal and clean slag.

The ores treated contain from 65 to 71 per cent. of tin. The usual charge is 4 tons of ore mixed with about 10·5 to 12 cwts. of carbon, ground coal, or anthracite, according to the richness of the ore in tin, and about 2·4 cwts. of dross from the refinery. When necessary, limestone or fluorspar may be added to facilitate the formation of a suitable slag.

The furnace being hot from the working of a previous charge, the damper is closed to avoid loss by dusting, and the new charge, which has been damped for the same reason, is shovelled in and spread over the bed, so that it is thickest near the fire-bridge. The damper is then opened, and the fire urged until the charge is in a state of fusion, when it is well rabbled. The fire is again made up, and after about one hour, when the charge is well melted, another rabbling takes place. After further firing, and when the reduced tin has separated from the slag, the taphole is opened and the tin run out into the float. As soon as all the tin is out of the furnace the taphole is temporarily stopped, while a launder is placed under it; it is then freely opened, and the slag runs out through the launder into sand moulds at the side of the furnace. The average time required for the working of a charge is 7½ to 8 hours. The products are ore metal containing about 99·5 per cent. of tin, and rich slag containing from 20 to 40 per cent. of tin.

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* *Proc. Inst. of Civil Eng.*, vol. cxxv., part III. McKillop, Paper on "Tin Smelting, Malay Peninsula."

The tin in the float, when sufficiently cool, is laded into iron moulds, and the metal sent to the refinery.

The next stage in the smelting operations is the treatment of the rich slag for the extraction of its tin. This is effected by smelting it, together with dross from the refining of slag tin, with scrap iron, anthracite, and coral ($CaCO_3$). The furnace used is the same as that for the ore smelting, but a new or newly repaired furnace is generally employed, as the very high temperature of the operation tends to increase the resistance of the bottom to the leakage of tin.

The charge is worked in a similar manner to the ore smelting with occasional rabbling, but at a higher temperature.

The products are rough metal and poor slag, the former being tapped into the float, and the latter into sand moulds.

The rough metal usually contains 95·5 per cent. of tin, and the poor slag 2·5 or more of tin, as silicate. The first two or three pigs of slag, however, contain also shots of the metal, and are put aside for further treatment as below, the other pigs being thrown away. The extraction of tin from the slag containing shots of tin is carried out by smelting it in the manner just described for the treatment of rich slag, but with anthracite only. The impure metal obtained contains only about 80·0 per cent. of tin, the remainder being iron.

The tin in the slag which is thrown away often reaches 5 per cent.

Three grades of metal are thus produced in the smelting operations. The ore metal, as already mentioned, goes direct to the refinery, but the rough metal, with only 95·5 per cent. of tin, and the metal from the second slag smelting, with only 80 0 per cent., are first melted in a smelting furnace at a low temperature, and kept molten whilst the dross is skimmed off from time to time. After this treatment the resulting metal will contain about 99·5 per cent. of tin, and is sent to the refinery (see "Refining," p. 526).

Tin Smelting in Cornwall.—As regards tin smelting in Cornwall, exact details of the furnaces and methods employed are wanting, as the smelters, by reason of the severe competition prevailing, endeavour, as far as possible, to avoid publication of their methods of procedure. The following may, however, be taken as representing generally Cornish practice :—

The tin smelters in Cornwall labour under the great disadvantage of insufficiency of local tinstone, and hence are largely dependent on imported ores, generally Bolivian, for their chief production of tin.

The smelting is carried out in reverberatory furnaces, which in essential features do not differ greatly from the furnaces of Pulo Brani. The working bed is of fire-brick laid on a bed of fire-clay 6 to 9 inches thick, resting on fire-tiles supported by transverse iron bars, which run right across the vault of the furnace; hence it cannot be dropped like that of the furnace just described.

Generally each furnace has its own chimney stack, about 50 feet in height.

The dressed ore, "black tin," smelted contains usually from 65 to 70 per cent. of tin, and the charges range from 2 to 3 tons, three charges, or in some cases four, being worked in twenty-four hours.

The consumption of coal is said to be 1 ton for each ton of ore.

The smelting charge consists of black tin mixed with 15 to 20 per cent. of culm, according to its richness, some tin-bearing products from other operations, a small amount of slaked lime, and sometimes a little fluorspar. The smelting is conducted in a similar manner to that at Pulo Brani already described. The charge having been spread over the bed of the furnace, is melted, a high temperature being employed, and then rabbled from time to time. After a final rabbling, it is allowed to rest, so that the tin may separate as completely as possible from the slag.

The slag, after having been thickened, if necessary, by the addition of a few shovelfuls of culm, is skimmed off through the working door. This slag is known as " pulled " slag, and the first skimmings are generally sufficiently clean to be thrown away. The other skimmings contain shots of metal, and are put aside for further treatment.

The metal is not usually skimmed clean, and the slag which is left runs out with the tin when the furnace is tapped, and forms a layer on the metal in the float. This slag is known as " glass " ; it is removed from the tin as soon as it has set, and is put aside for resmelting. After the " glass " has been removed the tin is allowed to stand, and the dross which forms is removed by repeated skimmings.

The metal is then laded into moulds. The resulting slabs or blocks, sometimes called " tappings," are more or less impure, and have to be refined.

The slags, which are iron silicates with some calcium silicate, containing over 5 per cent. of tin, are smelted in the ore furnace with lime, to which fluorspar is sometimes added.

Liverpool has become a more important tin-smelting centre than Cornwall, as imported ores are smelted there at the works of Messrs. Williams, Harvey & Co. and of the Penpoll Tin Smelting Co., Ltd.

Tin Smelting at Tostedt, Germany.—The ores are almost wholly Bolivian, and, as already pointed out, are often very impure. Some contain only 40 to 50 per cent. of tin, with varying but considerable amounts of Cu, Pb, Sb, As, and S, whilst others have about 67 per cent. of tin and little more than traces of these foreign elements. These various classes of ore are for the most part separately ground and roasted, special care being taken to expel as much of the As and S as possible.

The smelting charge is prepared by mixing the different classes of roasted ore in such proportions that it shall have a more or less determined composition.

Ground anthracite is used as the reducing agent, the amount varying from 12 to 20 per cent., according to the richness of the ore.

Lime is always added as a flux, so that, together with the iron oxide present, a satisfactory slag may be formed with the silica. The amount used is determined by the percentages of iron oxide and silica present, care being taken that neither it nor the silica shall be in excess, lest in the former case calcium stannate, and in the latter tin silicate may be largely formed, and loss of tin result.

The operation of smelting is conducted in reverberatory furnaces with beds of siliceous sand burnt in over a fire-brick bottom similar to those of copper furnaces. The largest furnaces have beds 23 feet long and 16½ feet wide, and it is said that the loss of tin in smelting is less in them than in those of smaller dimensions, and less fuel is required per ton of ore. The usual charge is composed of about 6,600 lbs. of roasted ores, 880 lbs. of lime, and 1,200 lbs. of anthracite. It is first moistened, then thrown into the furnace, and spread over the bed.

The work of smelting is conducted in the usual way—*i.e.*, melting with repeated rabbling, the tin being finally tapped into a float and the slag run into sand moulds. The crude tin goes to the refinery. The rich slags are resmelted in the same furnace used for ore smelting, and the resulting slag in a blast furnace.

*Perth Amboy, New Jersey.**—The American Smelting and Refining Company has erected a tin smelting plant here for the treatment of 1,200 tons of Bolivian concentrate (60 per cent.) per month.

A plan of the works is shown in Fig. 203. The first crude tin was tapped on 7th March, 1916. The equipment consists of two Wedge roasters, two reverberatory furnaces, a liquation furnace, poling and casting appliances, and an electrolytic refinery. After sampling, the ores are transferred by an elevator to the main receiving bin. This bin, built of steel, is a sixteen-sided polygon, with the lower portion in the form of a frustum of an inverted pyramid. It contains sixteen compartments, each having an 8-inch delivery pipe. Under the centre of the bin is a turntable and platform scale, upon which the car to receive the charges from the compartments is placed.

The mixed charge is then taken to one of the Wedge furnaces, where it is given a dead roast. The Wedge turnaces are 16 feet in diameter, have five hearths, and roast about 35 tons of concentrate in twenty-four hours. They are oil-fired. The roasted ore is taken to another sixteen-sided bin, arranged similarly to the receiving bin. In this bin are compartments containing limestone and anthracite crushed to $\frac{1}{8}$ inch. The smelting charges are made up here, transferred to a mixer, and thence to the smelting furnace bin. The smelting is carried out in reverberatory furnaces. These furnaces are 38 feet long by 12 feet wide (inside), are lined with fire-brick, and have a fire-brick bottom. The bottom slopes towards the taphole, which is at the side of the furnace approximately in the middle. The furnaces are fired with oil. There are four charging hoppers along the centre line of each furnace. The smelting charge is 15 tons, and consists of about 12 tons of roasted concentrate, and the necessary amount of crushed limestone and anthracite. The charge is rabbled when necessary, and when the tin has been reduced it is tapped into a settler. The settler is of mild steel lined with fire-brick, and is divided into two compartments by a partition wall, having an aperture at the bottom. On tapping the furnace this opening is kept closed until the first compartment is sufficiently filled with metal and slag, so that the slag will not pass through into the other compartment. The aperture is then opened and the tin permitted to collect in the larger compartment. The slag in the first compartment overflows into a slag car. The slag is broken up when cold and crushed to about $\frac{1}{8}$ inch. It may contain from 10 to 25 per cent. SnO_2. When sufficient has accumulated, it is smelted in one of the reverberatory furnaces.

After tapping out the tin, the furnace is again charged. Three or four charges are usually obtained in twenty-four hours. After cooling for a short time, the tin in the settler is tapped into a pot, taken to the anode casting department, and cast into bars. These bars of crude tin are then charged

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* R. H. Vail, *Eng. and Min. Journ.*, May, 1916.

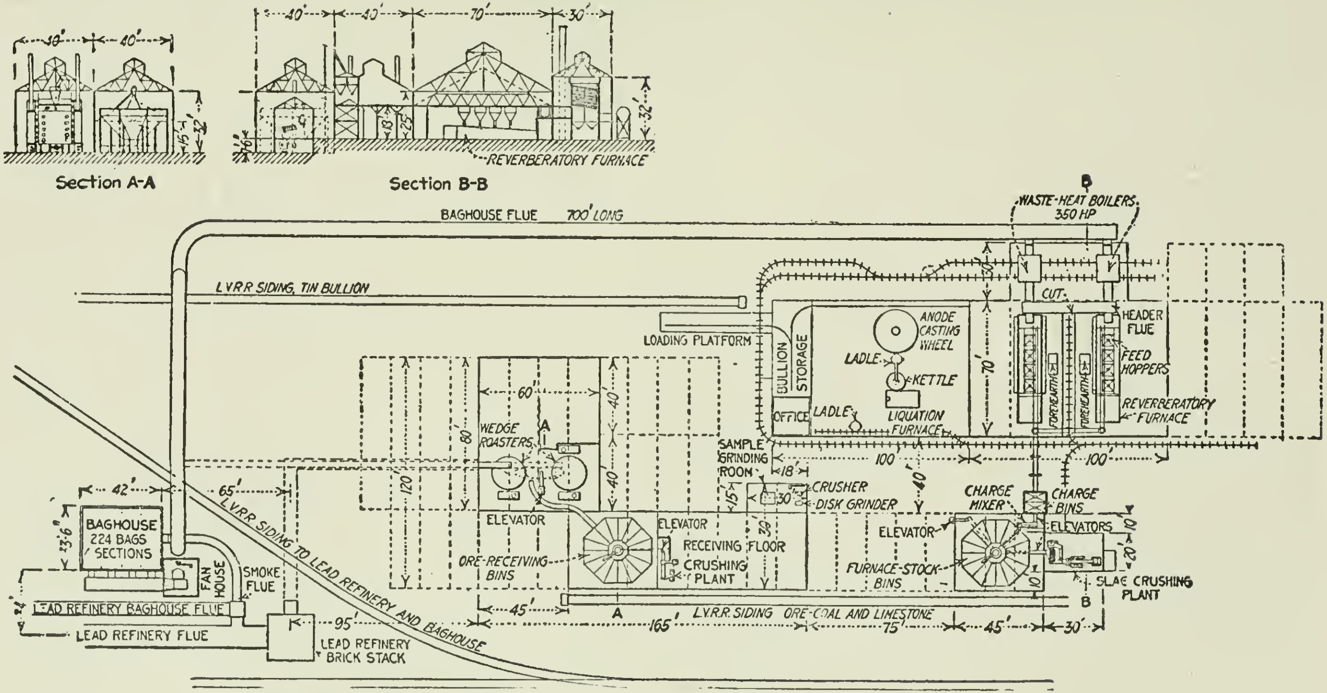
Section A-A
Section B-B
REVERBERATORY FURNACE
BAGHOUSE FLUE 700' LONG
WASTE-HEAT BOILERS, 350 HP
LVRR SIDING, TIN BULLION
LOADING PLATFORM
BULLION STORAGE
OFFICE
ANODE CASTING WHEEL
LADLE
KETTLE
LADLE
LIQUATION FURNACE
CUT.
HEADER FLUE
FEED HOPPERS
REVERBERATORY FURNACE
FOREHEARTH
FOREHEARTH
SAMPLE GRINDING ROOM
CRUSHER
DISK GRINDER
CHARGE MIXER
CHARGE BINS
ELEVATORS
SLAG CRUSHING PLANT
WEDGE ROASTERS
ELEVATOR
ORE-RECEIVING BINS
ELEVATOR
RECEIVING FLOOR
CRUSHING PLANT
ELEVATOR
FURNACE-STOCK BINS
BAGHOUSE 224 BAGS 7 SECTIONS
FAN HOUSE
SMOKE FLUE
LVRR SIDING TO LEAD REFINERY AND BAGHOUSE
LEAD REFINERY BAGHOUSE FLUE
LEAD REFINERY FLUE
LEAD REFINERY BRICK STACK
LVRR SIDING ORE-COAL AND LIMESTONE
A
B

Fig. 203.—Plan and Section of Tin-Smelting Works, Perth Amboy, New Jersey, U.S.A.

into a liquating furnace, the liquated tin being received in a pot 6 feet in diameter, set over its own fire. In this pot it is agitated by compressed air, which is equivalent to the old methods of poling or tossing, for from one to five hours. When the dross has been separated, the tin is skimmed clean, it is then fed by a centrifugal pump into a casting ladle, and cast into anode moulds on a casting wheel of the Walker type.

The gases from the reverberatory furnaces after heating two waste-heat boilers of 350 H.P. pass into a 7-foot steel flue for cooling, and thence into a bag-house containing 224 bags, 30 feet long, and 18 inches in diameter. The electrolytic refinery contains at present 68 vats similar in size and construction to those used in copper refining. The tanks are of wood lined with an asphalt coating. The electrolyte is mainly hydrofluosilicic acid of about 15 per cent. strength, in which is dissolved about 4 per cent. of tin. The cathode starting sheets are of tin about $\frac{1}{8}$ inch thick. The current density is about 12 ampères per square foot. The tin produced in the experimental plant has averaged from 99·96 to 99·98 per cent. Sn.

Blast Furnaces.—Blast furnaces are not employed in any of the chief works in Europe except, in some places, for the smelting of slags and residues, on account of the loss of tin by volatilization being greater than in reverberatory practice. Also because the tin produced by them tends to be very impure, owing to the high temperature causing a greater reduction of the foreign metals which may be present in the ore.

In Banca and Billiton, however, where the ores are rich and pure, blast furnaces only are in use. They are simple, low rectangular shaft furnaces of brickwork, generally 8 feet in total height and about 2 feet 5 inches by 2 feet 5 inches in cross-section. The blast is supplied by an ordinary fan, and enters the furnace through three tuyeres. The charge consists of alternate layers of ore and charcoal.

It is almost needless to point out that these furnaces are not suitable for tin smelting, except under the special conditions which are found in these localities. Rude primitive blast furnaces are also in use at small Chinese smelting works in the Malay Peninsula, as already stated.

Refining of Tin.—The crude tin obtained in the operations of smelting contains generally Fe as the chief impurity, and frequently Cu, Pb, As, Sb, etc.

The purity of the tin depends on the purity of the ore smelted, thus the very pure ores of Banca and Billiton often yield a metal containing 99·8 to 99·97 per cent. of tin, which does not require refining; in fact, is purer than much of that obtained elsewhere after refining. When the proportions of the impurities mentioned above are very small, not exceeding one- or two-tenths per cent., the metal may be remelted, allowed to stand molten for some time, when the upper portions can be laded into moulds for the market. Usually, however, the contaminating metals are present in larger amounts, and the metal has to be refined.

The process of refining consists of two operations:—

(*a*) Liquation, in which the chief portions of the iron, copper, and tungsten are separated.

(*b*) "Tossing," "poling," or "boiling." In these operations the metal is subjected to agitation, by which the remaining portions of the foreign metals are almost completely removed.

Liquation.—The operation of liquation, as applied in the refining process, is based on the fact that the alloys of tin with iron, arsenic, etc., are less fusible than tin. Consequently, if the impure tin is kept at a temperature just above the melting point of tin, these compounds will remain in a pasty or unfused condition, and the tin can be drained away from them. At Pulo Brani liquation is carried out in a small reverberatory furnace with a bed sloping downwards from the fire-bridge to the front door, outside which is a large float provided with a fire-place below it. The slabs of tin are placed on the upper part of the bed next the fire-bridge; a gentle fire is then kept up, the tin melts and drains away through the taphole into the float, leaving behind a residue consisting essentially of the less fusible alloys of iron and tin containing copper, arsenic, antimony, and sulphur.

Slabs of tin are fed into the furnace from time to time until from 6 to 10 tons of liquated metal are in the float. The fusible compounds of lead and bismuth have liquated with the tin, which also contains some iron, copper, etc.; it is hence further purified by the operation of "tossing." When the float is full the taphole is closed, the residue in the furnace melted, and when molten is tapped into another float, in which it separates into two portions, an upper, which is impure tin, and a lower, consisting chiefly of sulph-arsenide of iron and tin, termed "hardhead."

The hardhead produced at tin smelting works varies greatly in composition, according to the amount and nature of the impurities in the ore. Thus, in three typical samples the iron ranged from approximately 53 to 54 per cent., the tin from 18 to 36 per cent., the arsenic from 5 to 22 per cent., and the sulphur from 2 to 4 per cent.

It finds a ready sale, at a fair price considering its composition, for mixing with lead and antimony ores in smelting for the production of tin-lead and tin-antimony alloys (*Holloway*).*

In Cornwall the operation of liquation at some of the smelting works is performed in the same furnace in which the ore has been smelted.

At Tostedt (Germany), where the crude tin is obtained from the smelting of impure Bolivian ores, a reverberatory furnace of special construction is employed for liquation. The furnace is rectangular in section, with the fire-place at one end. The bed, which slopes uniformly from one of the long sides toward the other, is divided into three compartments, Nos. 1, 2, and 3, by low ridges, that next the fire-bridge, the hottest being No. 1, the middle one No. 2, and the other No. 3.

Each compartment has its own taphole. The dimensions of the bed are—length 18 feet, breadth 8 feet. In working a charge the crude tin is gradually fed upon the upper part of No. 2. The tin which liquates is received in moulds, charged into No. 3, the coolest compartment, and again liquated, whilst the residue in No. 2 is transferred to No. 1, the hottest compartment, and is there liquated. The liquated tin from the residue in No. 1 is then charged into No. 2 for reliquation, whilst the refractory residue, hardhead, is raked out. The tin obtained from No. 3 compartment is ready for poling, the residue going to No. 2.

In this furnace 3 tons of crude tin are thus treated in twenty-four hours.

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* *Trans. Inst. Min. and Met.*, vol. xviii., p. 477.

Poling, Boiling, or Tossing.—The object of these operations is the removal of the small amounts of the impurities, Fe, Wo, Cu, Bi, and Pb, which remain in the tin after liquation. It is effected by one or other of the methods described below, in which the molten tin is violently agitated, and every particle thus brought into contact with the air, when, in consequence of the large surface thus exposed, the impurities are oxidized together with some of the tin, forming a scoria, which, being lighter than the metal, floats on its surface, and is removed by skimming.

At Pulo Brani the operation of tossing is practised—*i.e.*, the tin is raised in ladles and poured from a considerable height, the metal being thus fairly well agitated. The liquated tin, after resting for about an hour in the float at the liquation furnace, is transferred by tossing to a series of four large pots, set about 2 feet below the float. If the metal, however, is not then sufficiently purified, it is subjected to the operation of poling, which is conducted in the ordinary manner.

At Perth Amboy agitation is effected by means of compressed air.

Poling or boiling, as generally practised, consists in plunging logs of green but not wet wood into the molten metal, contained in a pot known as a kettle, provided with its own fire-place. The logs are enclosed in two loops attached to an iron rod or frame, and are forced to the bottom of the kettle by a heavy weight fitted on the rod. The heat of the molten tin decomposes the wood, gases are given off together with steam, the contents of the kettle are thoroughly agitated, and every portion brought into contact with the air. The action of the steam is said to assist in the oxidation, but to what extent has not been determined. It is obvious that the duration of the operation will depend on the purity of the tin required.

After the poling is over, and the scoriæ have been removed, the metal is usually allowed to stand for some time at a temperature just above its melting point, to allow any heavy impurities to settle.

The upper portion, which is the purest, is ladled into moulds as refined tin, part of the remainder is cast as " block " tin, and the bottoms, when less pure, go back to the liquation furnace.

Care must be taken to avoid casting tin at too high or too low a temperature, or its brilliancy and whiteness will be impaired.

" Grain " tin is made by heating the pure refined ingots to a temperature just below their melting point, and allowing them to fall from a height when they break up into large irregular columnar crystals, or the ingots after heating are sometimes broken up with a heavy mallet.

Recovery of Tin from Tin Plate Scrap and Old Tinned Vessels.—Several methods have been employed, both electrolytic and chemical. The chief electrolytic method was based on the use of caustic soda as the electrolyte. It was attended with many difficulties, owing to the caustic soda rapidly becoming inactive through absorbing CO_2 from the air, the loose manner in which the scrap had to be packed, and the great care required in working to free the iron from tin to a sufficient extent to fit it for use in the manufacture of open-hearth steel.

Of the various chemical methods, the most successful is that devised by Dr. Goldschmidt, now carried on on a very large scale at Essen. In this process the scrap iron must be perfectly freed from moisture and organic matter, such as straw, paper, and varnish.

It is pressed into bundles, which are packed in baskets, and introduced into a large upright iron cylinder. The cylinder having been closed, chlorine is forced in under a pressure of about four atmospheres. Considerable heat is generated by the action of the chlorine on the tin, so that it is necessary to cool the cylinder in order to prevent the iron from being attacked. The gas is passed in until the tin is dissolved, which is known by the pressure remaining constant. The chlorine and tin chloride are removed from the cylinder by suction, and the residual iron is thoroughly washed with water.

NICKEL AND COBALT.

NICKEL.

Alloys of nickel have been known from very early times. They occur in old Bactrian coins of the year 235 B.C., composed of a copper-nickel alloy containing about Cu 77 to 78 per cent. and Ni 22 to 23 per cent.; also in ancient Chinese alloys. The metal itself was, however, only produced on a large scale in Europe early in the nineteenth century.

Physical Properties.—Nickel approaches silver in whiteness, but has a slight grey tinge, and is more brilliant than platinum. It welds readily, and can be welded to iron.

Malleability and Ductility.—In hardness cast nickel approaches soft steel. It is very malleable and ductile, and can be rolled into sheets of extreme thinness (0·0008 inch), also drawn into wire of remarkable tenuity (0·0004 inch diameter). Its malleability and ductility are diminished by the presence of C, Mn, As, S, and NiO.

Specific Gravity.—Its specific gravity when cast is 8·35, and when rolled or hammered 8·6 to 8·9, according to the mechanical treatment it has received.

Tenacity.—According to Kollmann, nickel containing 0·05 per cent. of magnesium has a tenacity of 38·9 tons per square inch, whilst, according to Shakell, the tenacity of wrought nickel, after annealing, is 42·4 tons per square inch.

Action of Heat.—The metal is difficultly fusible, its melting point being 1,452° C. (American Bureau of Standards), but, like iron, this is very considerably lowered by the presence of carbon.

When molten it absorbs CO, which is given off on cooling, unsound castings full of blowholes being produced. CO can also be generated in the molten metal by the action of carbon on nickel oxide, both of which it may contain. Nickel has also the power of dissolving its oxide just as copper dissolves Cu_2O, and with the same result, brittleness being produced. The unsoundness due to blowholes and the brittleness caused by NiO can, however, be removed by the addition of small quantities of magnesium to the molten metal, and perfectly sound and malleable castings be obtained. On heating commercial nickel in a vacuum, L. Guillet and A. Roux* obtained 22 times its volume of gas consisting of a mixture of H_2, CO, CO_2, N_2 and traces of CH_4.

Magnetic Properties.—Nickel is attracted by a magnet and becomes magnetic, its magnetic power, as compared with that of iron, being as 1 to 1·5, but at 340° C. it becomes non-magnetic.

Electrical Conductivity.—The electrical conductivity is about 12·9, if that of silver be taken as 100.

Atomic Weight.—The atomic weight of nickel is 58·68.

Chemical Properties.—Nickel in the massive state does not readily tarnish in the air at ordinary temperatures. At a red heat it becomes coated with the greyish-green oxide. It dissolves very slowly in hydrochloric and sulphuric acids, but is readily soluble in nitric acid and *aqua regia*. It resists very considerably the action of fused alkalies, hence the use of nickel crucibles for fusions in which sodium peroxide is used. The compounds of nickel, which

* *Compt. rend.*, 1926, vol. clxxxiii., p. 717.

are of the greatest importance in the metallurgy of the metal, are those which it forms with oxygen, silica, sulphur, arsenic, and carbon monoxide. There are two oxides, NiO and Ni_2O_3, but it is only the former that concerns us.

Nickel Oxide, NiO, has a greyish-green colour. It is this oxide which is formed when nickel sulphide or arsenide is roasted dead. Hydrogen reduces it at a red heat, and carbon and carbon monoxide at a temperature approaching whiteness. The following reactions, in which NiO takes part, are of great importance in the extraction of nickel from its ores :—

When NiO is heated with iron sulphide, nickel sulphide and ferrous oxide are formed ; similarly when heated with iron arsenide, nickel arsenide and ferrous oxide result. In either case, if silica is present, ferrous silicate will be formed, and the iron can thus be slagged off.

When NiO is heated with nickel sulphide there is no reaction, metallic nickel is not produced. As has already been mentioned, this oxide is dissolved by molten nickel.

It combines with silica to form silicates.

Nickel Silicate, Ni_2SiO_4.—There are several silicates, and all are reduced by carbon in the presence of bases which can unite with the silica. If they contain iron, part of the iron is reduced and alloys with the nickel.

When heated with metallic sulphides as pyrites, or with the alkaline sulphides, calcium sulphide, and the like, the nickel is converted into sulphide, and may thus be concentrated in a matte. As we shall see later, this is important in the smelting of garnierite. On the other hand, when nickel silicates are heated with arsenides, the nickel is only partly converted into arsenide.

Nickel Carbonyl, $Ni(CO)_4$.—Another important reaction in the metallurgy of nickel is the following :—

When carbon monoxide is passed over metallic nickel at temperatures between 50° to 150° C., gaseous nickel carbonyl is formed, which, on being heated to 180° C., is decomposed into Ni and CO.

This forms the basis of the Mond process for the extraction of the metal (see p. 544).

Nickel Sulphides, Ni_2S, Ni_3S_2. NiS, Ni_3S_4, NiS_2.—Nickel sulphides are not decomposed by carbon monoxide, and only slowly by carbon at a high temperature. They are soluble in nitric acid, and *aqua regia*, but not in hydrochloric or sulphuric acids.

Until the investigations of Bornemann, it was believed that nickel existed in mattes as NiS. The results obtained by him in 1907 show that NiS cannot exist under the conditions which prevail in the smelting of mattes. According to the amounts of Ni, Fe, and S present, the mattes contain combinations of Ni_2S with FeS, or of Ni_3S_2 with FeS, or free Ni_3S_2. If the proportion of S is small, a solution of Ni in Ni_3S_2 may be present. Bornemann proves, in fact, that the compound Ni_3S_2 represents the highest amount of S that can combine with nickel under the conditions of matte smelting, and that NiS does not exist in mattes.*

When nickel sulphides are roasted, part of the nickel and sulphur is oxidized, SO_2 being given off, and nickel oxide, nickel sulphate, and some unaltered nickel sulphides remain. By continuing the roasting at a higher temperature NiO alone is obtained.

* *Metallurgie*, 1908, vol. v., pp. 13 and 61.

If a mixture of nickel sulphides and iron sulphide be roasted dead, NiO and Fe_2O_3 are produced. If the roasting is only carried far enough to leave sufficient sulphur present to combine with the Ni, and if the roasted product is then fused with carbon and silica, the nickel will be obtained as sulphide (nickel matte), and the iron as a ferrous silicate slag. If an excess of sulphur is left in the roasted product, the nickel sulphide will contain iron sulphide, and a nickel-iron matte will be produced.

Similarly, if a mixture of nickel sulphide, iron sulphide, and copper sulphide be roasted so that just sufficient sulphur be left in the roasted product to combine with the copper and the nickel, a matte of copper and nickel sulphides will be obtained on smelting it with carbon and silica, and the iron will be removed as a ferrous silicate slag. If an excess of sulphur be left in the roasted product, then on subjecting it to fusion as above, part of the iron will enter the matte as FeS.

It may be repeated here that when nickel sulphides are heated with NiO no reaction takes place; it follows, therefore, that a pure nickel matte cannot be Bessemerized like a copper matte; on blowing air into it, nickel oxide is indeed formed, but being without action on the sulphide, it combines with any silica present, and forms slag. If, however, a nickel-iron or a nickel-copper-iron matte be Bessemerized, the iron can be removed, and a nickel matte or a nickel copper matte be obtained.

If a matte consisting of iron sulphide and copper and nickel sulphides be fused with sodium sulphate and carbon, or with sodium sulphide, the iron and copper sulphides will unite with the sodium sulphide to form a matte containing only a small quantity of nickel. The greater part of the nickel sulphides with some of the iron and copper sulphides form a separate matte. The first matte is more fusible and of less specific gravity than the latter, and floats upon it. so that they can be readily separated.

It is evident that by repeating this treatment of the nickel matte the copper and iron can be almost completely separated, and a more or less pure nickel sulphide can be produced.

Nickel Arsenides, Ni_2As, Ni_3As_2, NiAs, and $NiAs_2$.—Nickel has a great affinity for arsenic, and there are several arsenides, the chief metallurgical product containing them being known as nickel speise. Nickel speise is, however, of very variable composition, usually containing sulphur, cobalt, and often copper and iron. Two typical samples had the following compositions:—

Ni,	49·5	52·6
As,	37·8	34·1
Co,	3·2	3·3
Fe,	..	10·1
Cu,	1·6	..
S,	7·3	1·0

When nickel arsenides are roasted only part of the arsenic is expelled, arsenious oxide (As_4O_6) is given off, and nickel oxide is formed, but some of the As_4O_6 is oxidized to As_2O_5, and this combines with the nickel oxide to form an arsenate which is not decomposed by heat.

On mixing the charge with carbonaceous matter, this arsenate is partly reduced to arsenide, and on further subjecting this to oxidizing roasting more arsenic is expelled. By a succession of roastings with additions of carbonaceous matter most of the arsenic can be removed. The remaining arsenic is got rid of by fusion with nitre and soda, a soluble sodium arsenate being formed, which can be removed by lixiviation.

Nickel arsenide is usually associated, as we have seen, with iron, cobalt, and copper in nickel speise. When this is roasted a mixture of oxides, arsenates, and undecomposed arsenide results. If carbonaceous matter is stirred in, the iron arsenate is converted into Fe_2O_3.

In this connection it should be noted that nickel has a greater affinity than copper for arsenic, and copper than iron, whilst copper has a greater affinity for sulphur than for arsenic.

Hence, if the roasted material is smelted with coal and silica, and there is present sufficient arsenic to form Ni_2As with the whole of the nickel, the nickel will be obtained as an arsenide, and the iron will form a ferrous silicate slag. If cobalt is present, and there is sufficient arsenic to form Co_2As as well as Ni_2As, a nickel-cobalt arsenide will result, whilst if copper is present and sufficient arsenic be also present it too will enter into the arsenide. If there is an excess of arsenic, some of the iron also will similarly pass in.

If sulphur is present as well as copper in the roasted product of oxides. arsenates and arsenides, the copper will combine with it in preference to the arsenic forming a matte.

Commercial Nickel.—The nickel of commerce, with the exception of that obtained by the Mond process, is generally impure. It frequently contains only about 98·0 to 98·5 per cent. of nickel, often as much as 1·0 per cent. of cobalt, 0·3 to 0·6 per cent. of iron, a little copper, silicon, and magnesium. Arsenic, sulphur, and nickel oxide are also occasionally present; they cause brittleness in the metal and diminish or destroy its properties of being rolled or drawn. Even 0·1 per cent. of arsenic or sulphur is injurious. Iron, too, hardens nickel, and if much is present, say 1·0 per cent., the metal is unsuitable for the manufacture of the best qualities of German silver. As has already been pointed out, nickel dissolves carbon and also nickel oxide. With 1·0 per cent. of carbon it is brittle, but with a higher percentage it is tough. When, however, nickel contains both carbon and nickel oxide, carbon monoxide is produced on melting it, and the castings are full of blowholes. The nickel of commerce is usually in the form of small cubes, or in granules, the latter being sometimes known as "shot" nickel. The following are analyses of typical samples of commercial nickel:—

	Ni.	Co.	Fe.	Cu.	C.	S.	Si.	Mn.	Mg.
1. Mond nickel, .	99·78	..	0·161	0·015	0·06	nil	0·027 SiO_2	..	..
2. Special brand of nickel,	99·30	with some Co	0·39	0·07	0·09	0·01	0·14 SiO_2, Al, Ca	..	..
3. Average brand of nickel,	97·30	1·20	0·49	0·08	0·14	0·02	0·54 SiO_2, Al, Ca	..	..
4. Nickel from New Caledonian ore,	98·00	..	1·60	0·50	..	..	0·13	..	..
5. Nickel from New Caledonian ore,	98·23	..	0·98	..	0·50	..	0·30	..	..
6. One of the best brands,	99·10	0·04	0·30	..	0·05	..	0·10	0·05	..

1, 2, 3. Steinhart, "Metals and their Ferro Alloys," *Trans. Inst. Min. and Met.*, vol. xv., p. 234, *et seq.* 4 and 5. Moissan et Ouvrard, *Le Nickel*, p. 109.

The nickel produced by the Mond process is very pure, seldom containing less than 99·9 per cent. of the metal, with traces of carbon and iron.

According to recent specifications of the United States Government, the metal must contain not less than 97·0 per cent. of nickel.

Alloys.—The chief use of nickel is in the manufacture of nickel steel for armour plates, guns, and propeller shafts, etc., not less than about 60 per cent. of the world's production being thus consumed, whilst the remainder is principally employed as a constituent of alloys such as nickel silver, nickel coinages, and the like. and in electroplating.

In the manufacture of nickel and other special steels, the following alloys,[*] more particularly ferro-nickel, are made use of :—

Ferro-nickel containing from 25 to 75 per cent. nickel.
Tungsten nickel. ,, about 23 per cent. nickel and 73 per cent. tungsten.
Chrome nickel ,, ,, 23 ,, ,, 73 ,, chromium.
Molybdenum nickel containing from 20 to 50 per cent. nickel and 45 to 75 per cent. molybdenum.

An alloy of nickel and iron, called "platinite," containing 46 per cent. Ni and 0·15 per cent. C., has about the same coefficient of expansion as glass, and wires of the alloy, instead of platinum, are used for fusing into it.

Another nickel-iron alloy, named "invar," consists of steel with 36 per cent. Ni and 0·2 per cent. C. It has an extremely low coefficient of expansion, and is used in the manufacture of clocks, watches, scientific instruments, standard measures of length, etc.

An important alloy of nickel and copper to which the name "monel" metal has been applied is made by the Orford Copper Company by reducing the mixed oxides obtained by roasting nickel-copper matte from Sudbury ores without separation of the copper. It is also made by melting together its constituent metals. It consists of approximately Ni, 68 to 72 per cent. ; Fe, 0·5 to 1·5 per cent. ; C, ·073 to 0·15 per cent. ; S, 0·014 per cent., the remainder being copper.

Recent analyses by Parker are as follows :—[†]

	Shot used for Castings.	Bar ½ inch.	Bar ¾ inch.	Bar 1 inch.	Turbo-blading.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Nickel, . . .	67·10	65·87	66·03	66·03	67·10
Copper, . . .	29·00	27·81	27·55	28·53	27·00
Iron, ...	3·90	3·08	3·44	3·09	3·85
Manganese, . .	trace	2·38	2·38	1·82	1·87
Aluminium, . .	nil	0·37	0·26	0·18	..
Silicon, . . .	..	..	..	..	0·14

In the United States Government specifications, issued July, 1910, however, the following compositions are laid down :—

Monel-metal castings Ni 60 (minimum), Cu 33, Fe 6·5, Al 0·5, Pb nil.
,, rolled ,, 60 Cu 36, Fe 3·5, Al 0·5, Pb nil.

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[*] *Min. Ind.*, vol. x., p. 499.

[†] *Journ. Inst. Met.*, 1915, vol. xiv, p. 52.

The average tenacity of this alloy, as determined in twenty sand castings, was 35 tons per square inch, with an elongation of 38·5 per cent. on 2 inches, so that the metal approaches steel in these properties, whereas it is superior to steel in resisting corrosion. Propellers of "monel" metal have hence been fitted to several United States battleships, and to vessels of smaller size. It is also used for battery screens, and pump rods in mining, and many other purposes.

"According to Gaines,* the strength and other physical properties of the alloy are affected chiefly by the heat treatment, the variations in the proportions of the constituents within the limits in which they occur having comparatively little influence.

"Difficulty is sometimes encountered in obtaining sound castings of Monel metal, chiefly owing to dissolved oxides and gases, but an addition of 2 ozs. of magnesium per 100 lbs. of alloy before pouring is said to remedy the difficulties due to these causes.

"Owing to the remarkable resistance to corrosion shown by the nickel-copper alloys containing high percentages of nickel, attempts have naturally been made to adapt these alloys to various engineering purposes. If, for example, part of the nickel in an alloy similar to Monel metal is replaced by tin, the ductility of the alloy is lowered, but it possesses great resistance to corrosion, a low coefficient of friction, and is unaffected by moderately high temperatures. It is, therefore, a very valuable alloy for the construction of such parts as the seats and discs of high-pressure steam valves.

"An alloy for this purpose containing approximately 54 per cent. of nickel, 33 per cent. of copper, and 13 per cent. of tin, known as Platnam metal, is due to the enterprise of Messrs. J. Hopkinson & Co., who were the first to realize the importance of these alloys."

The copper-nickel alloys, in which copper is the chief constituent, are described under "Copper," p. 65.

"In the preparation of cupro-nickel alloys,† it is important that copper and nickel of good quality only shall be used. The alloy is made by melting the constituent metals together in the usual way in graphite crucibles, but considerable care is needed in its preparation, owing to the high melting point of nickel. Most of the difficulty is experienced in the casting shop. To ensure sound ingots, the metal must be poured 'hot' (about 1,300° C.), as unsound ingots result if the metal is cast at too low a temperature. The charge varies from about 80 lbs. to as much as 260 lbs., the average probably being about 120 lbs. Experience proves that large charges are to be deprecated. To ensure sound metal, it is necessary to add a small quantity of some deoxidizing agent, usually about 0·1 per cent. of manganese, to the molten metal shortly before pouring. The quantity of manganese to be added is 0·1 per cent. of the total weight of alloy melted, and not 0·1 per cent. of the nickel content only.

"A large variety of deoxidants is in use. Pure manganese is generally employed, but some manufacturers prefer cupro-manganese, consisting of copper 70 per cent. and manganese 30 per cent.

"Further, in the preparation of copper-nickel alloys, two special dangers present themselves, the first being the presence of oxygen, which renders the alloy brittle and practically useless for mechanical treatment, and the second the presence of carbon, for which nickel has an especial affinity. Oxygen is removed, as already mentioned, by a deoxidizing agent, such as manganese, ferro-manganese, copper-manganese, or magnesium, and the analysis of copper-nickel alloys should show small quantities (commonly 0·2 to 0·3 per cent.) of manganese or of magnesium.

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* Report of the Royal Ontario Nickel Commission, Ottawa, 1917, p. 333

† *Ibid.*, p. 327.

"Carbon up to a certain percentage is present as combined carbon, and as such appears to improve the working qualities of the alloy while worked cold, but as soon as the alloy is heated to about 650° or 700° C., especially over a long period, the carbon, which up to that temperature had been chemically combined, begins to segregate out as graphite."

"Nickel * is an important constituent of most of the base metal thermocouples now in use in pyrometric measurements.

"As a general rule, it may be taken that copper and 'constantan' (copper-nickel) couples, and iron and 'constantan' couples may be used for temperatures up to about 900° C., giving a very open scale. These couples give a high and very constant electro-motive force, and have the additional advantage of a small coefficient of resistance.

"For temperatures from 700° to 1,000° C., a nickel-chrome (10 per cent. chromium), known as Hoskin alloy, as positive element, in conjunction with an alloy of nickel containing small percentages of various other elements, is most suitable. Such a couple has an electro-motive force about 3·5 times that of platinum at 1,100° C."

Ores of Nickel.—The most important sources of nickel are the nickeliferous magnetic pyrites of Canada, and the hydrated nickel-magnesium silicate (garnierite) of New Caledonia; an insignificant amount is also obtained from the speises produced in copper and lead smelting, and from some copper mattes.

Garnierite.—A hydrous nickel-magnesium silicate, to which the formula $(NiMg)O, SiO_2 + xH_2O$ has been assigned; it is, however, very variable in composition. It occurs extensively in New Caledonia, and is free from sulphur, arsenic, and copper, but contains a little cobalt, seldom more than 0·6 per cent. CoO. There are two varieties, the green and the brown, the latter containing considerable amounts of Fe_2O_3. Rich specimens of the former may contain from 45 to 48 per cent., and of the latter 43 to 46 per cent. of NiO, but the average content of the ore shipped to Europe is only about 5·4 per cent. of nickel.

Nickeliferous Magnetic Pyrites.†—This ore, which occurs in large lenses of mixed pyrrotite and chalcopyrite at the contact of norite and granite or greenstone in the Sudbury area of Canada, provides about 90 per cent. of the nickel requirements of the world. The nickel-bearing mineral in these sulphide masses is *pentlandite* (FeNi)S; the proportion of nickel present varies from 1 to 5 per cent., and that of copper from 0·5 to 3 per cent., an average analysis of the ores from the mines showing about 3 per cent. of nickel and 1·6 per cent. of copper. In addition, the ores carry appreciable quantities of gold, silver and the platinum metals.

The discovery of these deposits was made in 1883, when the Canadian Pacific Railway was under construction. The pioneer company formed to work the ores was the Canadian Copper Company, which later became the International Nickel Company. The first ore mined was rich in copper and shipments were made to the Orford smelter in New Jersey, where difficulty was experienced in the smelting. This was found to be due to the presence of nickel, which was previously unsuspected.

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* *Ibid.*, p. 347.

† "The Copper-Nickel Industry of Ontario."—F. W. Gibson. Paper read before the *Third Triennial Empire Mining and Metallurgical Congress, S. Africa*, 1930.

Another company was formed by Messrs. H. H. Vivian & Co. of Swansea, which operated the Murray mine, a large deposit, the upper portion of which was somewhat low grade, but at depth the grade improved. The Vivians closed down the mine in 1894 and it eventually became the property of the British-American Nickel Corporation. In this company the British Government, during the European War, took considerable financial interest with the object of obtaining an independent source of nickel. Shortly after the close of the war, the British-American company ceased to operate, and the mine passed into the possession of the International Nickel Company.

The Mond Nickel Company was first interested in the Victoria mine and afterwards in the Lewack and the Worthington mines. Other companies entered the nickel field, but prior to 1928 the operating companies were reduced to two, namely the International and the Mond Nickel Companies.

In 1928, the International Nickel Company bought up the entire holdings of the Mond Company, and is now the owner of the assets of both companies. The fact that in the Frood mine there are large masses of ore running from 4 to 20 per cent. of copper and 3 to 4 per cent. of nickel, together with unusual values in the precious and rare metals, has changed the aspect of the Sudbury field, as nickel will no longer be the dominating metal, but will be replaced by copper, although the output of nickel will not be reduced.

The minerals proper of nickel are many, but none are of much industrial importance. The following may be mentioned as old and occasional sources of the metal :—

Kupfernickel (Nickel arsenide, NiAs).—It frequently contains iron, cobalt, and sulphur, and sometimes the arsenic is replaced by antimony up to half its amount. It was from this mineral that nickel was first isolated by Cronstedt. It occurs in Freiberg, Saxony, Austria, and France, and is still the source of a small quantity of nickel.

Cloanthite (White nickel ore, $NiAs_2$).—Frequently associated with the above.

Millerite (NiS).—It is only valuable for its association with magnetic pyrites, as in Sudbury ore.

Nickel Glance ($NiS_2 + NiAs_2$).—The above minerals, none of which occur in large quantities, were smelted in Germany, Austria, and Hungary, a speise containing nickel and some cobalt being obtained.

From the foregoing remarks it will be evident that the chief producers of nickel ores are Canada and New Caledonia. The chief producers of the metal, however, are not found in either, the ores or mattes being exported to other countries for its manufacture.

Extraction of Nickel from its Ores.—The most important methods carried on at present are the following, all of which are dry methods. In some cases, however, the concentrated product of smelting is subject to wet treatment and crude nickel is occasionally purified by a series of chemical operations. Electrolytic methods are also employed to a comparatively small extent in the United States and Germany :—

I. The extraction of nickel from sulphide ores.
II. ,, ,, ,, silicate ores.
III. ,, ,, ,, arsenide ores.
IV. ,, ,, ,, a product of I. by the nickel carbonyl or Mond process.

I. *Extraction of Nickel from Sulphide Ores.*—The ore treated is magnetic pyrites containing small proportions of nickel and copper.

If the ore contains no copper, the process is simplified, as we have then only to get rid of the iron, sulphur, and the gangue.

To accomplish this, the ore is roasted so that most of the sulphur is expelled, but sufficient must be left to combine with the whole of the nickel and also with part of the iron, otherwise some nickel will pass into the slag.

When the roasted ore is smelted a nickel-iron matte is obtained, and the gangue and most of the iron is removed as slag. The matte is called raw nickel matte. If poor in nickel it is roasted to oxidize more iron, and is smelted with silica in a shaft or reverberatory furnace. The Fe_2O_3 is reduced to FeO by the sulphur of the iron sulphide, in the presence of SiO_2, SO_2 is given off, and the FeO unites with the SiO_2, forming an iron silicate slag.

The concentrated matte will still contain iron sulphide ; it is hence melted in a reverberatory furnace, a blast of air being allowed to play upon its surface until the iron is oxidized and only a trace remains. The FeO combines with the SiO_2 of the furnace lining, and is removed as slag. Some of the nickel is also oxidized, and passes into the slag, so that this slag has to be returned to the blast furnace charges of the first smelting.

Instead of treating this matte in a reverberatory furnace, it may be freed from iron by Bessemerizing it in a converter. This is by far the best method in works where sufficient matte can be produced to keep a converter at work. A nickel matte containing but little iron will be obtained. The converter slag, like the reverberatory furnace slag, will contain too much nickel to be thrown away, and must be returned to the blast furnace to be resmelted.

As has been already pointed out, the nickel sulphide cannot be blown like copper sulphide to metal—*i.e.*, the sulphur cannot be oxidized or burnt off without oxidizing the nickel also—for NiO and Ni_3S_2 do not react to form metallic nickel.

Besides, the heat developed in Bessemerizing the matte is insufficient to fuse nickel. The nickel sulphide resulting from either the reverberatory furnace or the converter treatment is then roasted dead to nickel oxide, which may be reduced with carbon to metallic nickel in the manner to be subsequently described.

When the ore, magnetic pyrites, contains copper as well as nickel, as in Canada, the roasting must be conducted so that the sulphur in the roasted product must be sufficient to combine with the whole of the nickel and copper, and some of the iron when it is smelted with silica.

A Ni-Cu-Fe matte will then be formed. The iron may be separated from this matte in the manner just described by subjecting it to an oxidizing fusion in a reverberatory furnace or best by Bessemerizing it when a Cu-Ni matte will be obtained.

When this matte is roasted dead a mixture of copper and nickel oxide results, which may be reduced by carbon to form a Cu-Ni alloy that can be sold, if required, to manufacturers of German silver and Cu-Ni alloys generally. Owing to the small demand for this alloy, its manufacture was discontinued, but during recent years the Orford Copper Company, by a modification of the method of reduction of the mixed oxides, have produced an alloy of some importance, Monel metal (see p. 534). If pure nickel has to be prepared from the matte, the copper must be separated, and this is effected by melting the matte with sodium sulphate and coal, when the copper and any iron present unite with the Na_2S formed by the action of the coal on the Na_2SO_4, giving a very fusible matte of low specific gravity containing but little nickel, which separates from a less fusible matte of higher specific gravity rich in nickel and low in copper. By repeating this operation a nickel matte free from copper is obtained. The pure nickel sulphide is then roasted dead, and reduced with carbon as described, pp. 548 to 550.

The process, as carried on on a large scale for the extraction of nickel from Canadian ores, is hence rather complicated, owing to the presence of copper, which must be separated from the nickel if pure nickel has to be produced. The ore to be treated generally contains approximately nickel, 2 to 3 per cent.; copper, about 2 per cent.; iron, 45 to 60 per cent.; sulphur, 36 to 44 per cent.

The process consists of the following operations:—

1. Roasting in heaps.
2. Smelting the ore in blast furnaces for crude matte.
3. Concentration of the crude matte to a pure Cu-Ni matte with removal of the iron.

Either { 4. Roasting the purified matte dead.
{ 5. Reduction of the oxides and producing a Cu-Ni alloy.

Or 4*a*. Separation of the copper to obtain pure nickel sulphide.
5*a*. Roasting the nickel sulphide to NiO.
6. Reduction of the NiO to Ni.

The object is to produce at the first smelting a matte containing approximately 36 to 40 per cent. of copper and nickel, the remainder being iron and sulphur. The first operation is, therefore, the roasting of the ore to remove the excess of sulphur, and as there is no market for sulphuric acid, and there are no agricultural crops in the neighbourhood, no attempt is made to utilize the sulphur, so that the ore is roasted in heaps. Of course, sufficient sulphur must be left in the roasted product to combine with the whole of the nickel, copper, and any cobalt present, and with some of the iron, to prevent loss of the first-named metals in the slag.

The heaps are very large, usually 10 to 15 feet high, 80 to 110 feet long, and 50 feet broad, and hold from 1,000 to 3,000 or more tons of ore. In making a heap, a bed of about 9 inches thick of cord wood is first laid down, and upon it coarse ore is dumped from cars running on temporary trestles that extend over each heap. This is then covered with smalls, and finally with fines, the usual channels being left to facilitate the combustion of the wood and the oxidation of the sulphides. Each heap burns from two to four and sometimes five months.

The product of the roasting is a mixture of iron, copper, and nickel oxides, sulphates, and some undecomposed sulphides, in which the sulphur in the ore has been reduced to about 10 per cent., which is sufficient to combine with the nickel, copper, and some of the iron.

The reactions that occur in the operations are the same as those in the roasting of a pyritic copper ore, except that nickel sulphate requires a higher temperature for its decomposition than copper sulphate. The roasted ore is smelted in water-jacketed blast furnaces of the same construction as those employed in smelting copper ores.

Attempts have been made by the Canadian Copper Company to dispense with roasting and to treat the ore direct by pyritic smelting, but with little success.

The furnaces used by the Canadian Copper Company measure 50 inches by 204 inches, and a new one 50 by 255 inches, at the tuyere zone, those of the Ludwig Mond Company 50 inches by 240 inches. The charge consists of roasted ore to which raw ore is sometimes added. It should contain enough silica to combine with a sufficient amount of the iron oxide present, to ensure the concentration of the nickel and copper in a matte suitable for Bessemerizing. During the operation of smelting the nickel and copper oxides and sulphates become Cu_2S and Ni_3S_2 (Ni_2S according to Kern and Walter), and part of the iron oxide becomes FeS.

The FeS reacts with any copper or nickel silicates which may be present, converting them into sulphides, and thus prevents them from passing into the slag.

The composition of the matte varies according to the relative proportions of copper and nickel in the charge. Usually it contains 36 to 40 per cent. of copper and nickel, the nickel ranging from 15 to 25 per cent. At the works of the Canadian Copper Company an ore having copper 2 per cent., nickel 2 per cent., yielded a matte and a slag of the compositions given below :—

Matte.		*Slag.*	
Cu,	13·2 per cent.	SiO_2,	27·38 per cent.
Ni,	17·8 (Co 0·45) per cent.	FeO,	43·46 ,,
Fe,	42·0 per cent.	CaO,	2·5 ,,
S,	21·4 ,,	MgO,	10·0 ,,
		Al_2O_3,	2·0 ,,
		Cu,	0·4 ,,
		Ni,	0·3—4 ,,

The matte and slag flow continuously into settlers, from which the matte is tapped as required for the converters. The slag overflows into slag pots, by which it is conveyed to the dump, or, better, it is granulated and carried away by a stream of water.

The matte thus produced passes to the next stage of the process, in which the object is to diminish the iron, as far as possible, and obtain a matte consisting only of copper and nickel sulphides with not more than 0·3 per cent. of iron. This may be effected by three methods of treatment:—

(*a*) By roasting the matte and smelting the roasted product with silica in a blast furnace.

(*b*) By an oxidizing fusion in a reverberatory furnace.

(*c*) By Bessemerizing.

When the blast furnace matte is very poor in copper and nickel, and hence rich in iron, method (*a*) is sometimes followed, but the iron is only imperfectly removed.

If the crude matte contains the usual percentages of copper and nickel, but the production is small, method (*b*) is employed at some works. It has, however, the disadvantages of yielding a matte which will still contain 2 to 3 per cent. of iron, and entailing high costs for fuel and labour. It is conducted as follows:—

The furnace is practically the same as a copper-roaster furnace, with air ports and a sand bed, and the operations are based on similar principles. The object is the removal of the iron and some of the sulphur by oxidation, and the fluxing of the iron oxide by means of the SiO_2 of the furnace, or by the addition of quartz.

The unroasted matte is charged into the furnace in lumps and very slowly melted down at a low temperature with free exposure to the air entering the ports. After melting down, it is further oxidized, quartz is added to flux the FeO, and the operation is continued until only about 2 to 3 per cent. of the iron remains. The slag is skimmed off and the purified matte tapped out. The slag contains about 2 per cent. nickel, and goes to the blast furnace ore smelting. The process is sometimes repeated, and a matte containing only ·5 to ·75 per cent. of iron is obtained.

Method (*c*), Bessemerizing the crude matte in converters, is, however, undoubtedly the best, as by its means large quantities can be treated in the shortest time, and the refined matte is purer than that resulting from the other methods. It is, in fact, the method that is adopted at all the principal works.

The converters are all practically identical with those employed in copper converting, although their object is different, the concentration of the matte only being aimed at, and not its conversion into metal. The reasons why the copper nickel matte cannot be blown to metal have been already stated, but may be briefly repeated here. NiO and Ni_3S_2 do not react like Cu_2O and CuS to form metal, but the Ni_3S_2 is merely oxidized, and the resulting NiO combines with the silica of the converter lining, and passes into the slag. Further, if this reaction were possible, the temperature in the converter is insufficient to fuse metallic nickel.

Both acid and basic converters are in use, but the latter are gradually replacing the former.

Basic converters have been recently installed at the works of the Canadian Copper Company and the Mond Company.

The operation of Bessemerizing in an acid converter is carried on as follows:—The matte is tapped from the settler or melted in a cupola, and run into the converter, which has been turned down to receive it until it is nearly level with the spout. The blast is then started, and the converter turned up. After about thirty or forty minutes of blast the converter is turned down, and the first slag skimmed. The blowing is resumed and the converter turned up, and after about another forty minutes of blast, when the iron should be almost entirely removed, the slag is again skimmed off. When necessary, the blowing is continued until the iron is reduced to about 0·3 to 0·6 per cent. If the Bessemerized matte is in sufficient quantity it is poured into a ladle, to be cast usually into plates; if not, it is allowed to remain in the converter, a second lot of crude matte is run in, and the operation repeated. In some cases a third addition of crude matte is made, and the charge worked off before pouring. Quartz is sometimes charged into the converter to save the lining.

A sample of Bessemer matte produced at the old Mond Works at Victoria contained approximately nickel, 38 per cent.; copper, 41·5 per cent.; iron, 0·6 per cent.; sulphur, 18·5 per cent.

The converter slag varies in composition, according to the stage of the blow at which it is produced, thus the ordinary slag averages about copper 1·5 per cent., nickel 1·5 to 2·0 per cent., but during the last stages may contain copper 4 to 5 per cent., and nickel 17 or 18 per cent., these metals being partly present as silicates and partly as enclosed particles of matte. These slags are all returned to the blast furnace.

At the works of the Canadian Copper Company (Sudbury) the matte mentioned before (p. 540) contained after Bessemerizing about 44 per cent copper, 40 per cent. nickel.

At the Smelting Works of the Canadian Copper Company at Copper Cliff, Ontario, the matte produced by the blast furnaces had gradually become lower in copper and nickel and higher in iron than heretofore. The time required for a blow was greatly lengthened, and the destruction of the converter linings became exceedingly great, the old siliceous-lined converters have, therefore, been given up and replaced by large basic converters, 37 feet long by 12 feet in diameter, lined with magnesite.* The initial charge of the converter is about 60 tons of furnace matte, to which is added about 10 per cent. of dried quartz rock.

The blast is turned on for half to three-quarters of an hour, and the converter is then tilted to pour off the slag. Five or 6 tons of matte and 3 tons of quartz or siliceous ore are then introduced and the blowing is resumed. The cycle of blowing and addition of matte and flux is continued until from 70 to 80 tons of finished matte have accumulated in the converter. A period of thirty to fifty hours is required for working such a charge, during which 300 to 400 tons of furnace matte will have been treated. The slag contains less copper and nickel than in the acid plant. It is also lower in silica, which means economy of flux.

The gas † emerging from the converters averages about 14 per cent. sulphur dioxide and has been successfully used for the manufacture of sulphuric acid in a contact plant.

The purified matte obtained by Bessemerizing, or otherwise, is exported to the United States and to Wales, to be treated for the production of (*a*) a nickel-copper alloy, or (*b*) metallic nickel.

The treatment hence differs according to which of these products has to be obtained. If a nickel-copper alloy only is required, the process is simple, and consists merely of a roasting operation, to eliminate the sulphur and convert the Cu_2S and Ni_3S_2 into oxides, and to reduce them to metal by means of charcoal, or sometimes by reducing gases.

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* *Min. Mag.*, 1912, vol. vi., p. 380.

† W. H. de Blois, *Chem. and Ind.*, 1927, p. 257.

The Bessemerized matte is ground fine and is roasted dead in reverberatory furnaces, which may either be long-bedded calciners or short hand-worked calciners. Two roastings are necessary, the first of which may be carried out in the long-bedded calciner, and the second in the short furnace.

The product of the first roasting must be ground fine before treatment by the second roasting The mixed copper and nickel oxides are smelted with charcoal in a small blast furnace, when a fused alloy of copper and nickel containing small amounts of iron is obtained. It is by a modification of this process that the Ni-Cu alloy called " monel metal," described, p. 534, is prepared.

In order to obtain metallic nickel from the purified matte, there are two important processes, both complicated—viz., the Orford process and the Mond process.

The Orford Process.—In the Orford process the object is to separate the copper and the iron from the nickel in the matte and obtain pure nickel sulphide. This is effected as follows:—The matte is charged into a reverberatory furnace, lined with magnesite brick, together with crude sodium sulphate (salt cake) and coke, in the proportion of 6 tons of the sulphate and 1½ tons of coke to each 10 tons of matte. The charge, which usually contains about 50 tons of matte, is melted and kept molten for four or five hours, during which it is " poled " with green wood. The sodium sulphate becomes sodium sulphide by the action of the coke. Nearly complete solution of the copper and iron sulphide in the sodium sulphide is effected.

The charge may then be tapped into moulds, when it will separate into two layers, an upper layer consisting of sodium sulphide, containing nearly the whole of the copper and iron, and but little nickel, and a lower layer of nickel sulphide, containing but little copper and iron. To obtain pure nickel sulphide the operation is repeated. The upper layer is termed " tops," and the lower " bottoms " ; the process is hence known as top and bottom smelting. Blast furnaces were formerly employed for melting the charge, but reverberatory furnaces are more efficient.

In recent practice it has been found to be advantageous, and to give the best results, not to tap into moulds, but to allow the two mattes to separate in the furnace, and to tap them separately, either the top layer first, and afterwards the lower, or *vice versâ*. A more complete separation is thus obtained.*

Should the nickel sulphide not be sufficiently pure, the operation is repeated. On roasting this nickel sulphide dead nickel oxide is obtained suitable for reduction with charcoal to metallic nickel.

The concentrated matte may also be desulphurized by Borchers and Lehmer's process,† which consists in smelting it with lime and carbon in an electric furnace, when if the matte is free from other metals a fused pure nickel can be obtained.

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* *Eng. and Min. Journ.*, December, 1905, p. 1107.

† Borchers, *Hüttenwesen*, 1908, p. 121.

The Mond Process.—The Mond process depends on the remarkable property possessed by nickel of forming a volatile compound, nickel carbonyl ($Ni(CO)_4$) with carbon monoxide, which when heated to 180° C. deposits nickel in the state of metal.

The Bessemerised matte prepared at the works of the Mond Company at Sudbury is treated by this process at their works in Wales. Its composition is variable, but will approximate more or less closely to the following:—

Ni, ...	46 per cent.
Cu, ...	35 „
S, ...	18 „
Fe, ...	0·8 „
	99·8 „

The process consists of five operations, which are diagrammatically illustrated in Fig. 204.

(1) The matte is crushed, ground, and dead-roasted.

(2) The resulting oxides are treated with hot, dilute sulphuric acid, by which about 75 per cent. of the copper present is dissolved without taking up more than 1 or 2 per cent. of the nickel. The solution is taken to crystallizing vats, and copper sulphate obtained as crystals.

(3) The undissolved residue contains about 50 to 60 per cent. of nickel, and after drying is transferred to the reducing tower, where it is subjected to a carefully regulated reducing process by means of water gas.

The tower in which this is effected is provided with shelves; a temperature of 330° to 350° C. is maintained by a vertical gas-heated chamber which extends to the full height of the reducer and from which hot gases are made to circulate through a cylindrical heating box within each section. The roasted matte is stirred with mechanical rabbles, which, passing over the shelves, cause it to descend from one shelf to that below it, and finally to the conveyor, by which it is transferred to the volatilizing tower.

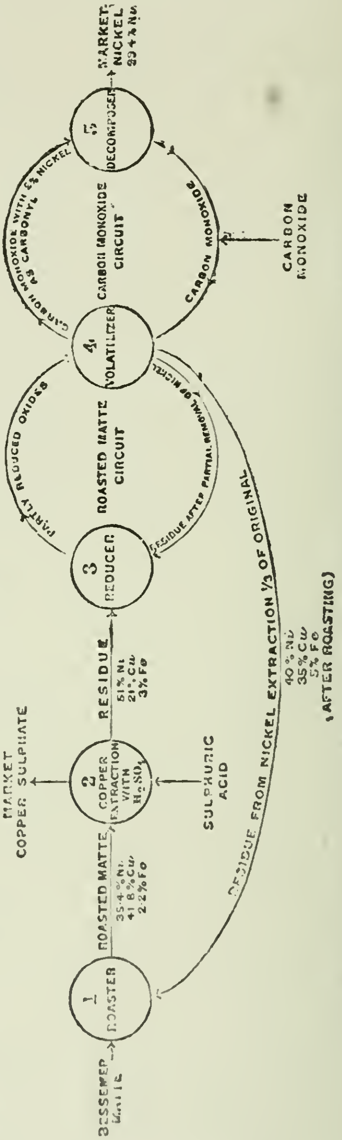
BESSEMER MATTE
1 ROASTER
ROASTED MATTE
35·4% Ni
41·8% Cu
2·2% Fe
2 COPPER EXTRACTION WITH H_2SO_4
SULPHURIC ACID
MARKET COPPER SULPHATE
RESIDUE
51% Ni
21% Cu
3% Fe
3 REDUCER
PARTLY REDUCED OXIDES
ROASTED MATTE CIRCUIT
RESIDUE AFTER PARTIAL REMOVAL OF NICKEL
4 VOLATILIZER
CARBON MONOXIDE WITH NICKEL AS CARBONYL
CARBON MONOXIDE CIRCUIT
CARBON MONOXIDE
CARBON MONOXIDE
5 DECOMPOSER
MARKET NICKEL 99+% Ni
RESIDUE FROM NICKEL EXTRACTION 1/3 OF ORIGINAL
40% Ni
35% Cu
5% Fe
(AFTER ROASTING)

Fig. 204.—Operations in the Mond Process. (Roberts-Austen, *Introduction to Metallurgy*, p. 442.)

(4) The volatilizing tower is similar to the reducing tower. No heating is necessary, the reaction $Ni + 4CO = Ni(CO)_4$ being exothermic. Heat is lost by radiation and the temperature is maintained at about 50° C.

From the volatilizer, the ore is returned to the reducer (3), and it continues to circulate between stages (3) and (4) for from seven to fifteen days, until about 60 per cent. of the nickel has been removed as nickel carbonyl. The residue is then returned to stage (1). The nickel carbonyl produced in this tower passes to the decomposer (5).

(5) The decomposer is a tower which is heated to a temperature of 180° C., so as to decompose the nickel carbonyl and release the nickel in the metallic form on granules of the metal.

CO is also released, and is returned to the volatilizer (4), to take up a fresh charge of nickel.

In order to prevent the granules from cohering they are kept slowly moving by withdrawing some of them from the bottom of the tower by means of a worm conveyor, which delivers them into two sifting drums. The small granules which pass through the sieves fall on to an elevator, by which they are returned to the top of the tower.

II. *Extraction of Nickel from Garnierite* (hydrated nickel-magnesium silicate).—The treatment practised for the extraction of the nickel in garnierite is much simpler than that followed for the sulphide ore of Sudbury, as it is free from copper and other metals except iron. The process, however, consists of six operations, viz. :—

1. Smelting with gypsum or alkali waste to obtain a Ni-Fe matte.
2. Partial roasting of the matte.
3. Smelting the roasted matte with silica to eliminate much of the iron.
4. Bessemerizing the matte produced to remove nearly the whole of the iron.
5. Dead roasting of the purified matte to convert it into nickel oxide.
6. Reduction of the nickel oxide with carbon.

It is obvious, therefore, that the extraction of the nickel depends in the first place on the affinity of the metal for sulphur, so that by one operation, that of smelting, as before, the nickel can be obtained in a nickel-iron matte, and the gangue of the ore can be got rid of as a slag containing so little nickel that it can be thrown away.

The ore as imported contains from 5 to 6 per cent. of nickel, associated with approximately SiO_2, 48 per cent. ; Fe_2O_3, 14 per cent. ; MgO, 15 per cent. ; H_2O combined, 10 per cent. ; and small amounts of Al_2O_3, MnO, etc.

It is smelted in water-jacketed blast furnaces, having been first mixed with alkali waste (chiefly calcium sulphide) or gypsum (calcium sulphate), in suitable proportions, for the production of a Ni-Fe matte and a slag sufficiently fluid and free from nickel. The mixture is frequently briquetted before being charged into the furnace. The matte is tapped from time to time, and is sometimes granulated to facilitate its preparation by grinding for the next stage of the process, whilst the slag flows out through the slag notch. The furnaces are small, smelting only about 30 to 40 tons of ore in twenty-four hours, with a consumption of 30 to 33 per cent. of coke.

The reactions which occur in the operation are simple ; the calcium sulphide of the charge or that produced by the action of the coke on the calcium sulphate reacts with the nickel silicate and the iron oxide yielding nickel and iron sulphides, which unite to form a Ni-Fe matte. The silica set free and that contained in the charge combine with the lime, magnesia, etc., to form a slag. The matte will usually contain 30 to 45 per cent. of nickel, and the slag 0·3 to 0·4 per cent.

The next or second stage of the process consists in the roasting of the ground matte in a reverberatory furnace, to oxidize part of the sulphur and iron, but to leave sufficient sulphur in the roasted product to yield a concentrated nickel-iron matte in the succeeding stage.

In Stage 3 the roasted material is smelted in a blast furnace with coke and siliceous sand and slags from Stage 4, by which the greater part of the iron is removed as a silicate slag, and a concentrated matte consisting of about Ni 65, Fe 15, and S 20 per. cent. is obtained. In the operation the slags produced contain 3 to 4 per cent. of nickel, and are returned to Stage 1.

Stage 4.—The concentrated matte is Bessemerized, the operation being conducted in exactly the same manner as that for the Cu-Ni-Fe matte from Sudbury ore, already described on p. 541, but in this case nickel sulphide is obtained. When the Bessemerizing has been properly carried out the resulting nickel sulphide will be nearly pure, containing only about 0·2 per cent. of iron. The slag contains much nickel, and is added to the charge in Stage 3. The nickel loss in the slag * is due partly to oxidation, but mainly to mechanical entanglement, and this is greater the more acid and hence more viscous the slag.

Stages 5 and 6.—The operations in these stages are also precisely the same as the corresponding operations in the treatment of Sudbury ore (pp. 543 and 548).

III. *Extraction of Nickel from Arsenical Ores.*—The smelting of arsenical ores is conducted on a very much smaller and less important scale than for those already dealt with, so that a less detailed description of the processes employed will suffice.

The arsenical ores, kupfernickel, cloanthite, etc. (see p. 537), contain often, besides arsenides, iron and other metallic sulphides. In the operations for their treatment the object is to separate the nickel from the iron, sulphur, arsenic, and gangue. The separation of the nickel from the iron is based on the greater affinity of arsenic for nickel than for iron, and the greater affinity of oxygen for iron than for nickel. It is hence possible to oxidize the iron and convert it into a slag by means of silica, and so remove it, whilst the nickel will combine with arsenic, and be obtained as speise. The speise is converted into nickel oxide by successive roastings and reductions, and finally by fusion with nitre. The oxide is then reduced with charcoal in the usual manner. The general scheme of treatment comprises the following operations :—

(1) Roasting the ore to eliminate most of the arsenic and sulphur, but leaving sufficient arsenic to combine with the nickel and some of the iron and sufficient sulphur to combine with any copper that may be present.

(2) Smelting the roasted ore with silica for the production of coarse speise, and a slag containing a considerable portion of the iron and the whole of the gangue of the ore.

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* B. Bogitch, *Compt. rend.*, 1926, vol. clxxxii., p. 1473.

(3) Roasting the coarse speise to oxidize as much as possible of the remaining iron.

(4) Smelting the roasted speise with silica, as in (2), but usually in a reverberatory furnace, to remove more iron and obtain a refined speise.

Generally the last two operations have to be repeated.

(5) Roasting the refined speise dead to obtain nickel oxide.

(6) Reduction of the nickel oxide with carbon in the usual manner.

(1) The ore is roasted in reverberatory furnaces or in muffle furnaces, when the arsenious oxide, As_4O_6 formed can be condensed and collected in suitable chambers. Care must be taken that the temperature must not be too high, or nickel silicates will be formed, which are with difficulty decomposed by arsenic, and nickel will pass into the slag in smelting. Also, there must remain in the roasted product 1 atom of arsenic to 2 atoms of nickel, otherwise nickel will enter the slag. The ore after roasting will consist of oxides, basic arsenates, sulphates, and undecomposed arsenides.

(2) The product from (1) is smelted in a blast furnace with the addition of sufficient silica to combine with the iron oxide and form a slag containing not less than 30 per cent. FeO. If less FeO is present, the slag will contain nickel, and also cobalt if the latter occurs in the ore. Any nickel silicate in the charge will pass for the most part into the slag. The products of the smelting are coarse speise, some copper matte if the ore contained copper, and a slag which is thrown away. If only a little copper is present it passes into the speise.

(3) The coarse speise is roasted in a reverberatory furnace to oxidize more of the iron.

(4) The roasted material is smelted as in (2). These two operations are repeated until the concentrated speise is sufficiently refined and poor in iron.

(5) The speise may now be roasted dead, finally with the addition of nitre in the manner described on p. 533, where the changes which occur in the operation are also explained.

(6) The resulting nickel oxide can be reduced to nickel with carbon as described, p. 548. The last operation is not generally performed, as any copper or iron present would pass into the nickel, but the refined speise, containing 50 to 70 per cent. nickel, is treated by wet methods for the extraction of the metal.

The composition of the speises which were obtained by treating an ore containing nickel 11·0 and cobalt 1·0 per cent. at Schladming* were as follows:—

	1st Speise.	2nd Speise.	3rd Speise.
Ni, ...	46	54	62
Co, ...	4	5	7
Fe, ...	8	4	2
Cu, ...	1	1·5	2
As, ...	33	34·5	27
S, ...	1	1	..

* Moissan et Ouvrard, *Le Nickel*, pp. 61 to 63.

Preparation of Pure Nickel from Speise (*Wet Method*).—The concentrated speise from operation (2), or the refined speise from operation (4), is roasted dead as in (5), to eliminate arsenic as much as possible. It is treated with hot hydrochloric acid, steam being passed in. The solution containing Ni, Co, Cu, Fe, and some As, much of the Fe being in the form of Fe_2O_3 remaining undissolved, is run into tubs after settling, sulphuretted hydrogen is passed in, and Cu, As, and any Bi or Sb present are precipitated.

The precipitated sulphides are separated by filtration, and the H_2S expelled from the solution by boiling it by the aid of steam pipes. The iron is then peroxidized with chloride of lime, and precipitated as ferric hydrate by milk of lime carefully added. Any arsenic remaining in the solution as As_2O_5 will also come down with the iron. Care must be taken to keep the solution below 40° C., or cobalt will be precipitated with the iron, and to avoid excess of lime, or nickel also will be precipitated. After separating the iron precipitate, chloride of lime is further added, the solution being heated to 40° C., and the cobalt is precipitated as Co_2O_3. The solution containing nickel is run off into another tank, in which milk of lime is added, and the nickel precipitated as hydrated oxide. The oxide is pumped into a filter press, washed, dried, and calcined. It is then reduced to metallic nickel, as described below. Every stage of the process requires extreme care.

The precipitated cobalt oxide may contain nickel; it is, therefore, redissolved in hydrochloric acid, the solution neutralized with milk of lime, and the cobalt reprecipitated with chloride of lime. The cobalt oxide is not reduced to metal, but is sent direct to market.

Sometimes the above treatment is varied and the iron precipitated before passing in sulphuretted hydrogen.

In such cases, after the sulphides have been precipitated, the filtered solution is successively mixed with iron, chalk, chloride of lime, and water, with a view to precipitate first any copper that may have passed into solution during filtration, and then the iron which has taken the place of the copper.

Reduction of Nickel Oxide.—On account of the high melting point of the metal, and as nickel oxide is reduced by carbon at a lower temperature, and further on economic grounds metallic nickel is generally prepared in the form of cubes, discs, grains, and spongy masses. In all these the nickel is a more or less close agglomeration of metallic particles, which contain all the impurities which have been present in the oxide and from 0·5 to 2 per cent. of carbon.

In America, however, the nickel oxide is reduced at a temperature above the melting point of the metal, so that molten nickel is obtained, and is cast in the form of small rods or is granulated.

In either case the nickel sulphide produced in the various processes described above is roasted dead by two roastings in the same manner as for the preparation of a copper-nickel alloy (p. 543).

In order to prepare cube-nickel from the nickel oxide thus produced, it is thoroughly mixed in a revolving or other mixer with flour and a little water to form a stiff paste. Sometimes sugar or molasses is used. The paste is then made into a thin rectangular cake, which after partial drying, to give it the proper consistence, is cut up with knives into small cubes. The cubes are then introduced, together with about 25 per cent. of their weight of charcoal in grains, into a series of fire-clay tubes, about 2 feet long and 8 inches in diameter, set vertically in a furnace chamber heated by gas. The tubes are open at both ends, and are prolonged below by iron tubes, 4 or 5 feet long, in which the cubes after reduction are cooled.

In working the furnace the tubes are first filled with coal or charcoal, and when sufficiently hot the cubes of nickel oxide and charcoal are fed in. The temperature is then raised to and kept at about 1,260° C.

From time to time a valve at the bottom of the iron tubes is opened, part of their contents of reduced cube nickel is withdrawn, and a corresponding number of cubes of nickel oxide and charcoal is fed into the upper opening of the fire-clay tubes. The operation is thus a continuous one. The cubes of nickel are then polished in a revolving iron drum.

The production of spongy nickel is carried on in crucibles heated in muffle furnaces, the charge being ground nickel oxide mixed with charcoal. To obtain a well-sintered and coherent product a temperature of 1,200° C. must be maintained for some hours.

Fused nickel is prepared at the works of the Orford Copper Company by heating the nickel oxide mixed with about 16 per cent. charcoal in plumbago crucibles in special crucible furnaces, in which petroleum, burnt by the aid of hot air, is used as fuel. The crucibles have a capacity of 75 lbs. of nickel oxide, and are set in pairs in each furnace. About four hours are required for reduction and melting. The molten nickel is usually cast in the form of small rods.

The nickel produced by the above methods is not very pure. It frequently contains only about 98 per cent. or rather more of nickel, with varying amounts of iron, carbon, nickel oxide, etc., and when fused is wanting in malleability and ductility.

As the separation of the impurities usually present is difficult, one of the chief aims in the processes for the extraction of the metal from its ores is to produce nickel oxide as pure as possible, so that the nickel obtained from it may not have to be treated for their removal.

Several methods have been proposed for the separation of impurities from the metal by oxidation whilst it is molten, but they do not appear to have been adopted in practical work, so that the usual procedure at present in treating crude nickel to obtain a malleable and ductile metal is based on the employment of reducing agents capable of decomposing carbon monoxide, nickel oxide, and cyanide. It has already been pointed out that carbon monoxide is absorbed by molten nickel, giving rise to vesicular castings; nickel oxide is dissolved, producing brittleness; and that sometimes nickel cyanide is present, also giving rise to brittleness. By the addition of magnesium all these are removed without the formation of any gas that will dissolve in the metal.

Not more than about 0·125 per cent. of magnesium is required. The nickel should be melted in plumbago crucibles with an inner lining or crucible of fire-clay, and the magnesium plunged well below the surface by means of a fire-clay receptacle at the end of a fire-clay rod. It must be cautiously added, otherwise explosions may occur. The nickel thus treated is malleable and ductile in a high degree. Aluminium and manganese are also employed, but they have less powerful action than magnesium; in fact, according to Wedding, magnesium is necessary if a compact forgeable metal is required.

When manganese is employed, the nickel is melted in a clay crucible with about 1·0 per cent. of the metal, whilst in some works manganese peroxide is mixed with the nickel oxide before reduction, when it is reduced to metal at the same time as the nickel.

If the nickel contains precious metals electrolysis is employed.

Electro-Metallurgy of Nickel.—According to Borchers, direct treatment of ore or even combined leaching and electrolysis are out of the question.

The following account of the electrolytic treatment of Bessemer matte for the extraction of metallic nickel is abstracted from the Report to the Canadian Government of the Royal Ontario Nickel Commission,* the Chairman of which was the late Mr. G. T. Holloway.

" The term ' refining ' is commonly employed in metallurgy to designate the final stages during which a crude metal is raised from, say, about 95 per cent. to ordinary pure metal. In the Report, however, the word refining is taken to cover the methods of producing nickel of good commercial quality from Bessemer matte, as that may be taken as the common meaning given to the term in the nickel industry, and invariably meant when considering that of Ontario.

" A considerable number of processes have been proposed for the electrolytic refining of nickel matte, and many have been tried and abandoned, often for reasons which it is difficult to understand, and which had apparently no direct connection with their actual merits or commercial prospects.

" Electrolytic treatment may be carried out on the unroasted or partly roasted matte, or on the matte after being roasted ' sweet '—*i.e.*, practically free from sulphur. The matte is commonly cast into anodes, or the solution obtained by treating the roasted or raw matte with acid or other solvents may be electrolyzed with the use of insoluble anodes, or, as is common, a combination of the two processes may be employed. Either the copper or the nickel may be deposited first, according to the conditions of deposition, voltage, etc., and a variety of solutions, of which sulphate, chloride, and cyanide are the principal, have been employed. It is common for nickel to accumulate in the copper solutions, so that electrolytic processes often yield not only metallic nickel and copper, but nickel salts, and could be arranged also to produce copper salts.

" Important features in favour of electrolytic refining are the small quantities of chemicals required, the absence of objectionable waste liquors, the ease with which further units can be added as increased output is required, the comparatively small losses of nickel and copper, and the practically complete recovery of the precious metals.

" The precious metals are a source of additional profit, and represent a considerably greater value than is generally supposed, although the amounts in the different mines vary greatly."

The Commissioners point out that the importance of the precious-metal contents of the Sudbury ores has not in the past been fully recognised. These consist of gold, silver, platinum, palladium, iridium, and the other rare elements. The proportions of these metals which the ores carry are minute, and appear to vary in the several deposits. Roasted matte from one of the companies showed 0·1235 oz. platinum and 0·197 oz. palladium, 0·027 oz.

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* Report of the Royal Ontario Nickel Commission, Ottawa, 1917.

gold, and 1·84 ozs. silver, while the other company's matte showed platinum, 0·988 oz.; palladium, 0·984 oz.; gold, 0·256 oz.; and silver, 6·155 ozs. per ton. The Orford refining process recovers a much smaller quantity of the precious metals than the Mond and electrolytic processes. The recovery of the metals of the platinum group constitutes an interesting chapter of the report. It states that the platinum and palladium contained in the Copper Cliff mattes for 1916 would be worth $794,600.

"The British America Nickel Corporation, Limited, intends to employ electrolysis for refining, and has made arrangements with Mr. Victor M. Hybinette, whose process is in successful operation in Norway on much poorer ores than any which are being worked in Ontario, for the sole use of this process in North America.

"The process actually employed at the Kristiansands refinery in Norway differs in some respects from these descriptions, but the main principles of the Hybinette method are therein set out.

"A member of the Commission was shown over the refinery of the Norwegian company, where the process is in full working operation. The following is as full a description of the process as the company is willing to have published, and although lacking in detail, may be taken as correctly outlining the process, and covering the general method of procedure.

The Hybinette Process.*—"The Bessemerized matte, obtained from the smelters at Evje and Ringerike, contains about 80 per cent. of nickel plus copper (commonly 47 per cent. of nickel and 32 to 34 per cent. of copper) with about 20 per cent. of sulphur and from under 0·25 to 0·4 per cent. of iron.

"The matte is received in a granulated form from the smelter, is roasted to remove the bulk of the sulphur, and leached with 10 per cent. sulphuric acid solution, whereby a large proportion of the copper with very little nickel is dissolved out, and the residue is melted down and cast into anodes about 3 feet by 3 feet 6 inches and nearly ½ inch thick. These anodes contain about 65 per cent. nickel and 3 to 8 per cent. sulphur, the remainder being copper with a trace of iron.

"The plants for depositing the nickel and copper are quite independent. The electrolyte used for the nickel carries 45 grammes of nickel and from 3 to 5 milligrammes of copper per litre, and is supplied by rubber tubes to the cathode diaphragms. After circulation, it contains from 2 to 3 grammes of copper per litre and is passed over waste anodes, which deposit the copper and re-supply nickel to the solution. The action of the anodes resembles that of pig iron in the cementation of ordinary copper, except that the copper is deposited by nickel instead of by iron. The amount of waste anode obtained during the electro-deposition of the nickel (about 30 to 40 per cent. of the original weight) is said to be about sufficient for the purpose of rejuvenating the exhausted solutions from the nickel vats, and it is stated that the solutions never require to be thrown away, as the cementation purifies them sufficiently.

"After the cementation, any waste anode fragments remaining after the cement copper has been cleaned off are crushed, roasted, leached with 10 per cent. sulphuric acid solution to remove more copper, as with the original matte, and the residues are melted into fresh anodes and re-electrolyzed.

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* See also F. E. Lathe, *Journ. Soc. Chem. Ind.*, 1925, vol. xliv., pp. 433T., 443T.; *Eng. and Min. J. Press*, 1925, vol. cxx., p. 5.

"The anodes for the nickel department are contained in special canvas bags obtained from Glasgow, and stated to last about 18 months. Paper diaphragms, supported by common canvas to prevent breakage, have been used when the supply of the special bags failed, and are said to have lasted as long as 12 months with careful handling.

"The nickel cathodes are made of iron plates rubbed over with a thin wash of water and graphite. The nickel is deposited on both sides of the plate, so that each gives two sheets of nickel. The plates, 3 by 3½ feet in area, are arranged in parallel, and the voltage depends on the number of tanks in operation; 3 to 4 volts per tank is used according to the current density, which is 8 to 10 ampères per square foot. Two kinds of tanks are used; large tanks, each containing 20 cathodes and 21 anodes, and smaller tanks containing 10 to 14 cathodes and 11 to 15 anodes—*i.e.*, in all cases, the number of anodes is one more than the number of cathodes. The nickel deposition takes about 10 days to complete. The deposited nickel weighs from 20 to 30 lbs. per sheet. The sheets of nickel are about ⅛ inch thick, and have the usual corrugated and warty appearance, but are dense, the corrugations and warty or stalactitic growths being normal, and giving no trouble as regards short circuiting. After being washed in weak sulphuric acid to remove basic salts, the sheets are dried and cut up into oblongs about 2 inches by 3 inches for sale. They are not melted down or otherwise treated, as they are said to be preferred by the German market in the flat as cut from the sheet.

"The metal is guaranteed 99 per cent. of nickel, but can be made purer. The copper does not exceed 0·1 per cent. (commonly as low as 0·03 per cent.), and the average iron content is 0·5 per cent. No attempt is made to remove the iron; the Bessemerized matte carries very little to begin with, although it contained as much as 2 to 3 per cent. in the early days. The small contents of iron and other impurities are, in fact, negligible, as the premium for pure nickel is very small.

"The precious metals become concentrated in the anode slime, which is melted up into fresh anodes and electrolysed separately, the final slime being sold direct for its precious metal contents.

"The copper is deposited very similarly to the nickel, but on copper sheets and without bags round the insoluble lead anodes. Anodes and cathodes are about the same size as for nickel. The copper takes about seven days for the deposition. The precious metals are obtained as in the case of nickel.

"The current density is about 10 ampères per square foot of cathode at 2 volts, and there are commonly nine cathodes and eight anodes per tank —*i.e.*, the reverse of the arrangement for the nickel deposition, in which the anodes exceed the cathodes by one in each tank.

"The refined copper carries about 0·10 per cent. graphite on the surface where stripped from the cathode."

The refining of metallic nickel containing the precious metals has been demonstrated by experiment to be feasible, and also the production of pure nickel from concentrated nickel matte, but the processes do not seem yet to have been employed on an extensive scale.

According to Borchers,* the conditions necessary for the electrolysis of nickel containing the precious metals are as follows :—

Electrolyzing tanks, made of wood with lead lining.

Anodes. Crude nickel, containing precious metals with up to 3 per cent. of sulphur, cast in plates.

Cathodes. Pure nickel.

Electrolyte. A solution of $NiSO_4$ or NiCl, the first being preferred.

Concentration. 30 to 100 grammes Ni, and not under 0·1 or over 2·5 grammes of free acid per litre.

Temperature. 50° to 90° C.

Current Density. 50 to 300 ampères per square metre.

Tension. 1 to 1·3 volts.

Reactions during the Process.—Under the foregoing conditions it is possible to produce even from crude nickel containing 0·5 per cent., a pure nickel not containing more than 0·1 to 0·2 per cent. of copper.

It is of importance that there should be enough sulphur present that the copper and iron may be converted into sulphides, whilst these sulphides in their turn unite to form compounds of $Cu_2S + FeS$. These compounds once formed are dissolved more slowly the lower the density of the current is at the anodes; it is necessary, therefore, that the anodes should have a notably larger surface than the cathodes.

Besides sulphur the crust will contain about 20 per cent. of mixed copper, nickel, and iron sulphides. The nickel obtained at the cathode will contain only very small amounts of copper.

Preparation of Ferro-Nickel from Sudbury Ores.—None of these methods has yet been carried out on a commercial scale.

It has been proposed to treat the Sudbury ore by the Longmaid-Henderson process (p. 158), to separate the copper, and to smelt the residue for the production of ferro-nickel. The process has, however, not passed beyond the experimental stage, and it has been pointed out that the residue from the ordinary run-of-mine ore would contain too much silica and too low a percentage of iron for smelting.

As regards the application of the electric furnace to the treatment of the Sudbury ores, it may be noted that "some are low in copper and high in iron, and, if these could be selected so as to contain only a minimum of copper, the large amount of iron present in the ore could be utilized directly to form ferro-nickel, and the costly separation of the copper could be avoided. This would, of course, be the ideal method to pursue, but the only attempt to put it into practice on a large scale, by the Lake Superior Power Company on Gertrude ore, proved a failure because of the presence of too much copper." †

EXAMPLES OF PRACTICE.

British America Nickel Corporation's New Works at Nickelton, Ontario.‡—The ore coming from the mine will be picked on picking belts and screened over $\frac{3}{4}$-inch grizzlies. The coarse ore will be smelted in blast furnaces to a 10 per cent. copper-nickel matte ; the fines will be added to the converter charge.

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* Borchers, *Hüttenwesen*, 1908, p. 122.

† Coleman, *op. cit.*, p. 132.

‡ E. P. Mathewson, *Eng. and Min. Journ.*, Aug. 1917.

The blast furnaces will be four in number, 25 feet in length by 50 inches wide at tuyeres, but so arranged that if necessary they can be coupled together to give nearly double the hearth area. These furnaces are to be charged from both sides, and will tap into the usual settlers, the slag being drawn off into slag cars and transported to the dump by electric locomotives.

The converter plant will be larger than usual, and will consist of seven of the latest type of Pierce-Smith converters, with shells 13 feet in diameter by 30 feet long outside measurements. These will be fitted with the Garr silica gun. A portion of the converter slag will be cast on the converter floor, broken up, and used in the blast furnaces as flux. The remainder will be poured into the blast furnace forehearths for settlement. The converter matte produced will contain about 80 per cent. copper and nickel, approximately 1 per cent. iron, the remainder being mostly sulphur. This will be granulated and taken to the refinery, where it will be roasted in mechanical furnaces of the Wedge type, then leached to extract the bulk of the copper, which will be recovered electrolytically, using insoluble anodes. The residue from the leaching will be melted down and cast into anodes, which will be electrolyzed by the Hybinette process.

Fig. 204*a* gives a clear idea of the lay-out of the plant. Sufficient room has been left for extension in all departments. The smeltery building proper will be 160 feet wide and 360 feet long ; the refinery building 225 feet wide by 400 feet long. In addition to these buildings there will be provided shops, change-house, club-house, laboratory, general office, warehouse, power-house, sub-station, etc.

The capacity of the plant to be installed will be about 2,500 tons of ore per day, or a nickel production of 10,000 tons per annum.

Power will be secured from the Hydro-Electric Company of Ontario, and all machinery will be operated by electricity. However, a steam plant of about 1,000 H.P. will be required to heat the various buildings and solutions. Steam-generator sets will be used as pressure reducers, the electricity to be used in connection with the main power plant, and also for emergency purposes. The main power plant will consist of steam-generator sets, turbo-blowers, electrically driven for both converters and blast furnaces, air compressors, motor generator sets, etc. About 10,000 E.H.P. will be necessary for the operation of the plant.

The new nickel-copper smelter was blown in on January 17th, 1920. By January 20th the first blast furnace to be fired had attained the daily capacity of 660 tons of charge.

The Canadian Copper Company, Copper Cliff, Ontario.*—There are five blast furnaces, 50 by 204 inches inside at the tuyeres, and a new one somewhat larger, 50 by 255 inches. The water jackets are in two tiers, the lower being 8 feet and the upper 6 feet 4 inches high.

The dust chamber is of $\frac{5}{16}$-steel plate of the balloon type, 20 feet wide, 34 feet high, and 500 feet long, supported on steel columns. The bottom has hoppers and clean-out doors every 6 feet. The stack is 210 feet high and 15 feet inside diameter at the top. The roasted ore is taken from the

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* A. P. Coleman, *The Nickel Industry*, Government Printing Bureau, Ottawa, 1913, p. 138, *et seq.*

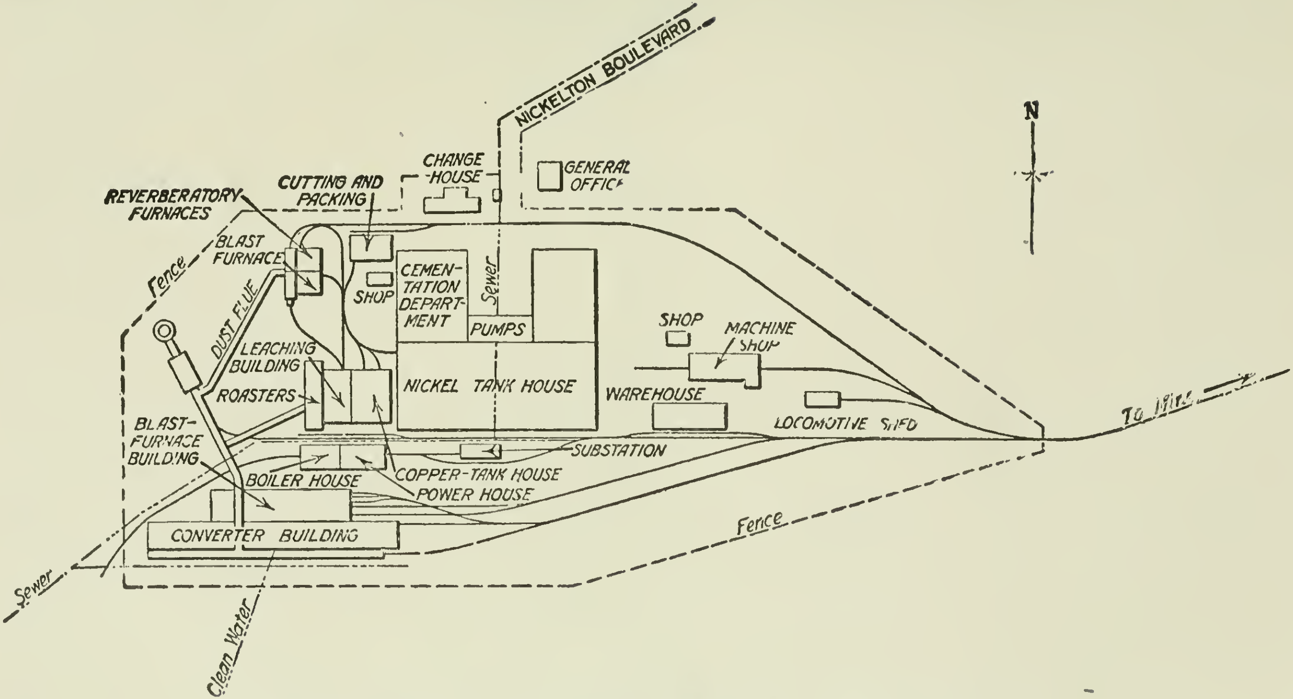
NICKELTON BOULEVARD
N
CHANGE HOUSE
GENERAL OFFICE
CUTTING AND PACKING
REVERBERATORY FURNACES
BLAST FURNACE
Fence
DUST FLUE
SHOP
CEMENTATION DEPARTMENT
Sewer
PUMPS
LEACHING BUILDING
ROASTERS
NICKEL TANK HOUSE
SHOP
MACHINE SHOP
WAREHOUSE
LOCOMOTIVE SHED
To Mine
BLAST-FURNACE BUILDING
SUBSTATION
BOILER HOUSE
COPPER-TANK HOUSE
POWER HOUSE
CONVERTER BUILDING
Fence
Sewer
Clean Water

Fig. 204*a*.—Plan of New Works, British America Nickel Corporation at Nickelton, Ont.

roast heaps by a steam shovel, placed in drop-bottom 50-ton cars, which deliver to the ore bins, from which the furnaces are supplied. A charge consists of about 10,000 lbs. of roasted ore, containing 10 or 11 per cent. of sulphur, 2,000 or 3,000 lbs. of raw ore low in sulphur, and 10 to 12 per cent. of coke. About 2,000 lbs. of quartz are added as flux. The coke is charged in first, then the ore and flux, and then some scrap or floor screenings. The blast is normally 24,000 cubic feet of air per furnace, at about 25 to 35 ozs. pressure. The settler for receiving the matte and slag is oval in shape, having diameters of 16 feet and 19 feet 6 inches. The matte from the settlers is tapped into 7-ton steel ladles, clay-lined, and taken to the converter building. The slag overflows into 25-ton slag cars, and is taken to the dump.

The smelting requires great care to ensure a matte of about 20 per cent. to be dealt with by the five converters. A comparison of the amount of work necessary to convert matte of different grades into Bessemer matte is given by Mr. Browne, as follows :—

To make 100 tons of Bessemer matte per day.

A 10 per cent.	furnace	matte would	require	14	basic converters.
18	,,	,,	,,	7	,,
20	,,	,,	,,	5	,,
25	,,	,,	,,	4	,,
30	,,	,,	,,	3	,,

In the converter department, there are three basic converters, 37 feet 2 inches long by 10 inches in diameter outside measurement. There are 44 tuyeres, $1\frac{1}{4}$ inches in diameter and 7 inches apart. The charge and working of the converter has been already described (p. 542). The flue dust, and the ore fines from the mines which is too small for the blast furnaces, are smelted in two large reverberatory furnaces together with converter slag. These furnaces have hearths 112 feet long and 19 feet wide, the bottom being of magnesite brick. They are interesting, as being the first reverberatory furnaces to be fired with powdered coal.

The Mond Nickel Company, Coniston, Ontario.*—The ores mined are nickeliferous pyrrhotites containing some chalcopyrite ; they contain about 2·3 per cent. Ni and 1·75 per cent. Cu, besides small amounts of Au, Ag, Pt, and Pd.

In the main smelting building are two blast furnaces and two Pierce-Smith basic converters, provision being made for an additional blast furnace when required.

The blast furnaces measure 240 inches by 50 inches at the tuyeres, and 69 inches at the top of the jackets, and each is provided with a crucible of structural steel lined with chromite bricks, and a brick top above a single tier of water jackets.

Each furnace is carried on structural steel columns, the jackets being hung from I-beams. The crucible rests on three rows of nine supporting columns, 5 feet in height; it consists of a rectangular steel I-beam frame about 6 feet in width, 21 feet 9 inches in length, and 25 inches deep. This crucible frame is lined with chrome brick around the sides, ends, and bottom, reducing the internal width to 4 feet 2 inches. The sole plate is of cast iron in four sections.

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* *Eng. and Min. Journ.*, Dec. 1914. (Excerpt from "The Copper Smelting Industries of Canada," by A. W. G. Wilson.)

The height of the furnace from this plate to the level of the charging floor is 19 feet. Above the crucible there is a single tier of water jackets, eight on each side, 8 feet 2 inches in height.

The furnace has 32 tuyeres 4 inches in diameter, 16 on each side, the blast pressure being about 38 ozs. The throat of the furnace above the water jackets is built of ordinary brick lined with firebrick. The top of the brickwork on the long sides of the furnace is 3 feet 7 inches below the charging floor, and this space is bridged with inclined apron plates. The brickwork at the ends is carried up to 8 feet above the charging floor, and above it is an iron hood. A gooseneck, 7 feet 6 inches in diameter, connects with the main flue, and a straight stack, closed by a damper, rises 15 feet above the hood.

The settlers are circular, 15 feet in diameter. The dust chamber is 50 feet long by 30 feet broad. It is connected with the furnaces by a steel flue rectangular in section, 10 feet by 15 feet, having hoppers for the collection and discharge of the dust arranged in sets of two along its base. Similar hoppers are fitted to the bottom of the dust chamber. In the converting department are two basic converters of the Pierce-Smith type, 25 feet 10 inches long and 10 feet in diameter. The lining of each shell consists of 16-inch silica brick and 9-inch magnesite brick at the bottom; 9-inch magnesite brick at the top, and at the tuyeres, special 18-inch magnesite brick. Each shell is provided with 30 tuyeres. None is placed below the " stack " or opening for the discharge of the gases, but 14 on one side and 16 on the other. The " stack " is on one side of the median tire, its centre being 11 feet 2 inches from the end of the shell. The pouring spout is 7 feet 7 inches from the same end. The shell is supported by three steel tires resting on pairs of carrying rollers. Rotation is effected by means of steel ropes, pulled by a sliding gear operated by an electric motor and a worm screw with an 8 feet stroke.

Two 50-ton cranes are provided in the department.

COBALT.

Physical Properties.—Cobalt is a grey metal with a slight reddish tint, and takes a high polish. It is attracted by the magnet, and is the most magnetic metal after iron. In hardness and tenacity it exceeds iron.

Cobalt is considerably harder than nickel, its hardness being about 124 on the Brinell scale, whereas that of nickel is only about 76·4.

It is magnetic at all temperatures up to about 1,110° C.

It can be welded to iron and steel.

Malleability and Ductility.—It can be hammered and rolled hot, but at ordinary temperatures it is hard and brittle.

*Tenacity.**—Its tenacity as cast and unannealed is about 34,400 lbs. per square inch, but the metal is brittle. The addition of carbon raises the tenacity, and with other impurities, such as iron, greatly increases the percentage reduction and elongation.

Commercial cobalt, when 0·25 per cent. of carbon is present, has a tenacity of 61,900 lbs. per square inch, and is fairly ductile.

Density.—The density of cobalt when unannealed is 8·7918, and when annealed 8·8105 (*Kalmus* amd *Harper*).

Action of Heat.—Cobalt melts at 1,478° C.—that is, at about 50° C. lower than iron (*Burgess* and *Weltenberg*).

Electrical Resistance.—Approximately five times that of pure copper.

Atomic Weight 58·97.

Chemical Properties.—Cobalt is not altered by air or water at ordinary temperatures.

It is slowly soluble in hydrochloric and sulphuric acids, but quickly in nitric acid.

There are three oxides, the most important being cobalto-cobaltic oxide, Co_3O_4.

This oxide is prepared from ores or speises containing cobalt, also Ni, Cu, Fe, As, S, etc. They are first roasted to eliminate the greater part of the As and S, and to convert the metals, as far as possible, into oxides. The roasted product is then treated by wet methods, as described under nickel (p. 548). Considerable quantities of the oxide are now being produced in the Cobalt district, Ontario. Metallic cobalt may be made from this oxide by reduction with carbon, carbon monoxide, hydrogen, or with aluminium. It is used largely in the preparation of the following colouring materials and pigments :—

Smalt, a silicate of potassium and cobalt, containing 6 to 16 per cent. Co ; 56 to 70 per cent. SiO_2, the remainder being K_2O. It is, however, very variable in composition.

Thenard's Blue.—Cobalt ultramarine, a mixture of cobalt oxide and alumina, said to be one of the most permanent blue pigments.

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* H. T. Kalmus, *Report on Cobalt and its Alloys*, to the Canadian Department of Mines, Government Printing Bureau, Ottawa.

Rinmann's green, a mixture of zinc oxide and cobalt oxide.

The manufacture of these belongs rather to chemical than metallurgical works.

Cobalt Ores.—The most important are the following :—

Smaltine or Tin-white Cobalt, $CoAs_2$.—Rarely found pure, almost always containing Ni and Fe. The chief localities are Saxony and Bohemia. It is also one of the chief cobalt minerals at Cobalt, Ontario.

Cobaltine or Cobalt Glance, CoAsS.—Sulph-arsenide of cobalt, in which part of the cobalt is usually replaced by Fe and Ni.

Localities.—Sweden and Norway, also met with in Rajputana, India, and is a common mineral of the deposits of Cobalt.

Asbolan—Earthy Cobalt.—A wad in which oxide of cobalt is associated with manganese peroxide and ferric hydrate. The proportion of cobalt ranges from 2 to 20 per cent. It occurs in considerable quantities in New Caledonia, and is also found in Spain.

The most important ores at present containing cobalt are those of the Cobalt district, Ontario, Canada. They consist of arsenides of cobalt and nickel, native silver, and silver sulphide and sulph-arsenides. They contain from 9 to 18 per cent. of cobalt, but are most important for their great richness in silver.

Mispickel sometimes contains 5 or 10 per cent. of cobalt.

The chief sources of the supply of cobalt until recently were the complex arsenides of cobalt and nickel of Saxony and Silesia, the asbolan of New Caledonia, and the speises and some mattes obtained in smelting the ores of other metals, especially of those containing nickel, with which cobalt is almost always associated. But since the discovery of the Cobalt district, Ontario, where cobaltiferous ores occur on a very extensive scale, the cobalt-bearing material produced there exceeds many times the annual consumption of cobalt oxide.

Most of the mines on the Cobalt field, Ontario, supplement hand-sorting by wet gravity methods of concentration, and flotation methods are also used.

Treatment of Ores.—At Deloro, Canada, the crushed ore is mixed with the necessary fluxes and smelted in a low pressure blast furnace, with the production of crude silver bottoms, speiss and slag. The speiss is crushed, calcined in coal-fired reverberatory furnaces and then given a chloridising roast.

From the roasted material, silver is extracted by means of sodium cyanide solution, from which it is precipitated by means of powdered aluminium. The residual oxides are dissolved in hydrochloric acid and the solution neutralised with ground calcium carbonate, which causes the precipitation of iron and arsenic as light-brown ferric arsenate. Calcium hypochlorite (bleaching powder) is then added to the solution containing cobalt and nickel, black hydroxide of cobalt, $Co(OH)_3$, being precipitated. This precipitate is removed before the whole of the cobalt comes down and then the precipitation of the remaining cobalt is continued, a quantity of black nickel hydroxide $Ni(OH)_3$ being precipitated at the same time. This intermediate product is retreated and the nickel remaining in solution is precipitated as nickel hydroxide by means of lime or as nickel carbonate by means of sodium carbonate.

The black hydroxide of cobalt is dried and ignited for the production of oxide, which is then reduced.

The Metal Cobalt.—The metal can be prepared by heating the oxide, Co_3O_4, with carbon by the methods followed for the preparation of nickel (see p. 548).

When it is prepared by reducing the oxide in a crucible with powdered anthracite a temperature of 1,200° C. is necessary, but when powdered charcoal is used as the reducing agent, the reduction is effected at a somewhat lower temperature. The product will contain about ·2 per cent. of the carbon (*Kalmus*).

When the oxide is reduced by means of aluminium, the metal will be free from carbon and may contain less than 0·1 per cent. of aluminium.

When carbon monoxide is used as the reducing agent, complete reduction is effected at 900° C. or a little above, but the charge must be completely cooled in an atmosphere of CO. It is suggested by Kalmus that where producer gas is available it should offer a cheap and efficient means of producing large quantities of pure metallic cobalt from the oxide.*

Uses.—The addition of cobalt to iron has been found to afford important magnetic properties. Permanent magnets are made of steel containing cobalt in addition to tungsten and chromium, *e.g.*, Co 34-40 per cent., W 5-9 per cent., Cr 1·5-3 per cent., C 0·4-0·8 per cent.

Its alloys with chromium and tungsten, and with chromium, tungsten, and molybdenum, to which the name "stellite" has been given, possess remarkable mechanical properties.† The material requires no heat treatment. It is cast to size and shape, and is simply ground to a cutting edge. The alloy consisting of 55 cobalt, 15 chromium, 25 tungsten, and 5 molybdenum, when made into high-speed cutting tools, is said to increase the speed of cutting 50 to 100 per cent. as compared with the best grade of high-speed tool steel.

The addition of 0·5 per cent. cobalt to an 80/20 brass is said to increase the tensile strength by about 18 per cent.‡

Another application of cobalt which is likely to become important is its use for electro-plating instead of nickel. This has been included in the series of researches on the metal by the Canadian Department of Mines.§

The results of the researches show that cobalt can be deposited on brass, iron, steel, copper, tin, German silver, lead, and Britannia metal; that the deposits are firm, adherent, hard, and uniform, and can be readily buffed to a satisfactorily finished surface. The cobalt deposited is much harder than nickel, and the speed of deposition is very much greater.

The deposits stand satisfactorily all the usual bending, hammering, and burnishing tests. The actual weight of cobalt required for a good coating is about a quarter that of nickel. The whole working should, therefore, be more economical.

According to A. Levasseur,‖ a suitable solution for electro-plating contains 300 grammes of anhydrous cobalt sulphate per litre with additions of sodium chloride and boric acid (as in a nickel bath), and a current density of 100 to 160 ampères per sq. ft. may be used.

The uses of the oxide have already been stated.

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* Kalmus, *op. cit.*

† *Journ. Iron and Steel Inst.*, vol. lxxxviii., p. 668.

‡ Browne, *Trans. American Inst. of Metals*, 1914, vol. vii., p. 61.

§ *Op. cit.*

‖ *Brass World*, 1926, vol. xxii., p. 303.

ANTIMONY.

Physical Properties.—Antimony is a brilliant white metal with a bluish tinge and a crystalline structure. When allowed to cool slowly it has a markedly foliated structure, and if its upper surface has been covered with a slag of special composition, it will present a characteristic fern-like pattern, which is called the "star," hence the name "star antimony" applied to the refined metal. A distinct and well-formed "star" is generally considered to be an indication of the purity of the metal, yet it must be remembered that, although this appearance cannot be produced in impure antimony, it is not found in the pure metal either, unless it has been covered during solidification with the above mentioned slag.

Malleability and Ductility.—Antimony does not possess these properties in the slightest degree; in fact, it is so brittle that it can be easily powdered in a mortar.

Specific Gravity.—Its specific gravity is 6·71.

Action of Heat.—The melting point of antimony is 630° C. It volatilizes at about 1,500° C.

Electrical Conductivity.—Antimony is a poor conductor of electricity, its conductivity being only 4·2 if that of silver be taken as 100.

Atomic Weight.—The atomic weight of antimony is 120·2.

Chemical Properties.—Antimony is not acted on by air at ordinary temperatures, but when heated to redness in an open vessel antimonious oxide (Sb_4O_6), which is volatile, is formed.

Antimony is only attacked by hydrochloric acid when it is in fine powder. It is not acted on by dilute sulphuric acid, but the hot concentrated acid dissolves it, producing an antimony sulphate, SO_2 being evolved. It is oxidized by nitric acid, the dilute acid converting it into antimony trioxide (Sb_4O_6), or a mixture of this oxide with the pentoxide (Sb_2O_5), while the strong acid oxidizes it chiefly to pentoxide.

Aqua regia dissolves antimony readily with formation of antimony pentachloride ($SbCl_5$).

With hydrogen it forms antimoniuretted hydrogen (SbH_3), as, for example, when zinc containing antimony is treated with dilute sulphuric acid, or when a soluble salt of the metal is introduced into a mixture generating hydrogen.

Oxides of Antimony.—Three oxides are known—the trioxide (Sb_4O_6), tetroxide (Sb_2O_4), and the pentoxide (Sb_2O_5).

The trioxide (Sb_4O_6), antimonious oxide, is a white powder when cold, yellow when hot, produced when antimony is burned in the air, and when antimony trisulphide is roasted. It is fusible at a red heat, and will volatilize unchanged if air is excluded, but with free admission of air it is oxidized to tetroxide (Sb_2O_4), which is infusible and non-volatile. This latter property, as we shall see later, is important in the roasting of antimony sulphide ores.

The trioxide is soluble in hydrochloric and tartaric acids, and in solutions of the caustic alkalies. It is reduced to the metallic state when heated with carbon or with potassium cyanide.

The tetroxide (Sb_2O_4), an infusible, non-volatile, white powder. It is produced when antimony or antimony trisulphide is heated with free access of air. When fused with antimony trisulphide, SO_2 is given off, and the trioxide is formed, which combines with some of the trisulphide, forming a fusible compound called " antimony glass."

When heated with carbon only partial reduction to metal occurs, Sb_4O_6 is chiefly produced, and is volatilized. If, however, it is heated with carbon and alkaline carbonates it is reduced to metal.

Antimony pentoxide, Sb_2O_3, is of no metallurgical interest.

Antimony Sulphides.—There are two sulphides, the trisulphide (Sb_2S_3) and the pentasulphide (Sb_2S_5), the former alone being of metallurgical importance.

Antimony trisulphide occurs native as stibnite, the chief ore of antimony. It is fusible at a red heat, and at a white heat can be volatilized.

Hydrochloric acid dissolves it, $SbCl_3$ being formed. When antimony sulphide or ores containing it are roasted in reverberatory furnaces antimony trioxide and sulphur dioxide are formed. The trioxide is partly volatilized and partly converted into the non-volatile tetroxide. No antimony sulphate is produced.

If the antimony sulphide be roasted with limited admission of air the antimony is volatilized as trioxide, and on this property depends the process of " volatilizing roasting " as applied to poor ores and liquation residues in the extraction of their metal (p. 576).

The trisulphide is difficult to roast on account of its fusibility, its melting point being about 550° C., and its tendency to form fusible " antimony glass," as described below. Advantage is taken of its fusibility in separating it by liquation from the gangue with which it is associated in ores.

Antimony sulphide is decomposed at a red heat by hydrogen, potassium cyanide, zinc, and iron, the last reaction being specially important, as it is utilized in the English method of extracting the metal.

It is not reduced by carbon at ordinary furnace temperatures.

When antimony trisulphide and antimony trioxide are heated together under a flux there is no reduction to metal, they simply melt, forming " antimony glass," a very fusible compound, which seriously interferes with the roasting of stibnite. On the other hand, when heated together in a current of inert gas they yield metal and SO_2 (*Schoeller*). If the trisulphide be fused with alkalies or alkaline sulphides, sulph-antimonides are formed, which are soluble in water, a reaction which has been made use of in the electro-metallurgical treatment of ores.

Commercial Antimony.—The commercial nomenclature of antimony and its products is apt to be confusing to those who are not directly concerned with them, thus :—

" Crude antimony " does not mean impure antimony, but the liquated sulphide.

" Needle antimony " is a term sometimes applied to the liquated sulphide.

" Regulus of antimony " is the metallic antimony of commerce, although it may contain but little sulphur or impurities,

" Star metal " or " star antimony " is the finest quality of refined antimony.

The refined metal or " star antimony," as met with on the market, usually contains small amounts of iron, sulphur, and lead, and occasionally arsenic and copper. They tend to increase the blue tinge of the metal. The best brands of the "star" metal are generally guaranteed to contain 99·6 per cent. antimony.

The following analyses of refined antimony are given by Pautrat (*Revue de Chemie Industrielle*, March, 1907):—

Sb,	99·450	99·690
S,	·069	·075
Fe,	·190	·070
Pb,	trace	·081
As,	·265	trace
SO_2,	trace	·008
	99·974	99·924

W. A. Cowan, in a paper presented at the meeting of the American Institute of Metals, September 7-11, 1914, gave the following analyses of ingots of antimony bought in the market, as follows:—Cookson's, branded "C"; Hallett's, branded "H"; Japanese, branded MC; and Chinese, branded with two overlapping circles. Each sample was analyzed by two independent chemists. Their results were as follows:—*

	Cookson's. Per cent.		Hallett's. Per cent.		Japanese. Per cent.		Chinese. Per cent.	
	A	D	A	D	A	D	A	D
Lead,	0·041	0·102	0·669	0·718	0·443	0·424	0·018	0·029
Tin,	0·035	trace	0·175	0·012	0·175	0·012	0·035	none
Arsenic,	trace	0·092	trace	0·210	0·008	0·095	0·017	0·090
Bismuth,	..	none	..	none	..	none	none	none
Copper,	0·040	0·046	0·038	0·046	0·034	0·043	0·008	0·012
Cadmium,	..	none	..	none	..	none	..	none
Iron,	0·010	0·004	0·014	0·007	0·015	0·007	0·007	0·004
Zinc,	trace	0·034	trace	0·023	trace	0·023	trace	0·027
Ni and Co,	..	0·028	..	none	..	none	..	trace
Sulphur,	..	0·086	..	0·128	..	0·201	..	0·078
Antimony,†	..	99·608	..	98·856	..	99·195	..	99·760
Total,	..	100·000	..	100·000	..	100·000	..	100·000

In other brands the percentage of antimony may be only 99·0 or less. In these the common impurities will range approximately as follows:—

Fe, 0·1 to 0·2; S, 0·07 to 0·15; Pb, 0·1 to 0·2; As, trace to 0·1.

The metal is sold in the form of cakes or discs, or of fragments of them, all having the fern-leaf markings or "star" on their upper surfaces, as mentioned above.

The value of any sample of antimony is judged by buyers generally not by analysis, but by its appearance, and a good sample of metal should exhibit the following characteristics:—

The star should be bold and defined, standing well up on the metal, the edges of the ridges sharp and straight. The metal itself should be lustrous and white, not dull and leaden looking. Lastly, on breaking the ingot, the crystals should be large and their surfaces free from specks, which are a sign of sulphur in the metal, a most undesirable impurity. On this last point perhaps more than many others depends the value placed on the sample under consideration.*

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* *Eng. and Min. Journ.*, Dec. 1914.

† By difference.

Uses.—Owing to its physical properties, especially its brittleness, pure antimony cannot be employed for any useful industrial purpose. It is, however, very extensively used in the manufacture of alloys, and this is by far the most important application of the metal.

The oxide and sulphides are used as pigments, and as these have been recognized by the French and Italian Governments as being non-poisonous, and hence superior to lead pigments in this respect, their use will doubtless largely increase. The vulcanizing of india-rubber also absorbs a considerable amount of the sulphide.

In the preparation of pharmaceutical products and of enamels some antimony is consumed.

Alloys.—Antimony alloys readily with a number of metals, but with very few exceptions it is seldom the chief constituent of any industrial alloy, as all alloys containing over about 30·0 per cent. of the metal are wanting in useful physical properties. Its effects when added to metals, even in small amounts, are generally to induce brittleness, and hence to diminish their malleability and ductility. When added, however, in proper proportions to certain alloys, it confers on them valuable properties. Thus, in the case of the lead-tin alloys it enables them to expand in the act of solidification, hence their value in type founding, where accurate casts of letters have to be produced.

In others, as in Britannia metal, a tin-antimony alloy, the addition of antimony to tin gives hardness to the metal without destroying its malleability, and enables it to receive a bright and durable polish. The most important alloys of which it forms an essential constituent are the various kinds of bearing or antifriction metal, type metal, and Britannia metal. Descriptions of these alloys will be found under "Lead," p. 180, and "Tin," pp. 512-515.

It is an important constituent of shrapnel bullets.

A beautiful crystalline alloy, of a fine violet colour, known as "regulus of Venus," is obtained by melting together equal parts of copper and antimony.

Ores of Antimony.—*Stibnite*, also known as antimonite, antimony glance, and grey antimony ore, is the native trisulphide Sb_2S_3, and contains when pure 71·77 per cent. Sb.

It is very widely distributed, and forms the most important ore and chief source of the metal, but is only found in workable quantities in comparatively few localities. The countries in which it occurs on the largest scale, and in which the principal mines are situated are China, France and Bolivia. Other mines of less importance are in Italy, Spain, Portugal, Mexico, Algeria, Australia, and California.

It is a dark grey mineral, which occurs as compact or coarsely crystalline masses in lodes or veins nearly always associated with eruptive rocks.† Antimony lodes are usually simple in character, with no considerable extension either in depth or along the strike. The average width of the lodes is about one foot, and few lodes are as much as a yard in width.

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* E. Rodger, *Journ. Soc. Chem. Ind.*, vol. xi., p. 19.

† *The Mineral Industry of the British Empire and Foreign Countries*, Imperial Mineral Resources Bureau, 1921.

Unless the ore is associated with gold, silver, or some other mineral of economic value, it does not form a satisfactory basis for extensive mining operations. The minerals usually associated with antimony ore are arsenical pyrites, galena, copper pyrites, iron pyrites and ores of gold, silver and mercury. Gold is so frequently associated with antimony that the ore should always be assayed for it.

When prepared for the market, antimony ores should be as free as possible from such deleterious impurities as lead, copper, arsenic and bismuth. The limits allowed are 0·1 per cent. each of arsenic and copper, and 0·2 per cent. of lead.

Antimony Trioxide (Sb_4O_6) occurs native in two forms, the rhombic valentinite and the cubic senarmontite. They occur in the gossans and upper parts of the deposits of stibnite, and are the results of its oxidation. The latter is an important ore in Algeria. The tetroxide (Sb_2O_4), cervantite, also a product of the weathering of stibnite, is found, but only in small unimportant quantities, in Italy and Spain.

In addition to the above, there are numerous minerals of antimony, or of which antimony is a constituent, but they are of mineralogical interest only.

Another, but indirect, source of antimony is the lead obtained from antimonial lead ores, especially in Spain, the by-products from the refining of this metal yielding "hard" lead, which is used in the manufacture of antifriction metal and other antimonial alloys.

Extraction of Antimony from its Ore.—Dry methods only are employed for the extraction of antimony from its ores. Attempts have indeed been made with a view to extract the metal by wet and by electrolytic processes, yet so far none of these processes has been adopted in practical work on a commercial scale. The dry methods may be classified as follows :—

I. Liquation of stibnite in order to separate antimony trisulphide from the gangue of the ores and obtain "crude antimony" (liquated sulphide).

II. Treatment of rich stibnite or of the liquated sulphide in order to obtain metallic antimony (antimony regulus). The so-called "precipitation" or "iron reduction" process.

III. Smelting in blast furnaces.

IV. Treatment of poor stibnite ores by roasting or by volatilizing-roasting for the production respectively of antimony tetroxide and antimony trioxide.

V. Reduction of these oxides and of oxide ores to metallic antimony (antimony regulus).

VI. Refining the impure metal for the production of "star" antimony.

It need hardly be emphasized that, whatever smelting operations are carried out, a perfect flue system and an efficient condensing plant should be provided.

I. *Liquation of Stibnite for the Production of "Crude Antimony" (Antimony Trisulphide).*—The process consists in subjecting the ore to the action of heat in such a manner that the fusible trisulphide will melt and liquate from the gangue.

Liquation is now chiefly carried on in remote places, mainly in order to obtain a concentrated product which can be transported at less cost than the ore to localities where it is treated for the production of metallic antimony. The process is a wasteful one, unless the residue, which always contains a considerable amount of antimony up to 15 per cent., or even more, is worked up; it is hence highly probable that it will be given up in all but exceptional places, and the ore be treated for the production of metal at the mines. There is, however, a large demand at present in England, Germany, and elsewhere for the liquated sulphide or, as it is called, "crude antimony," and so long as this demand exists, and a satisfactory price is obtained for it, it will continue to be produced.

One of the most important and successful mining companies in China liquates its medium grade ore (50 to 55 per cent. Sb) and exports the crude antimony, while it treats the liquation residues, together with the low-grade ores, by the French process of volatilizing-roasting.

Rich stibnite containing over 90 per cent. trisulphide is not liquated. It is either ground and sold for the manufacture of paint, or it is treated direct by the English precipitation process or by the reverberatory precipitation process. Stibnite containing less than 90 per cent. trisulphide and as low as 40 per cent. is liquated.

As the sulphide has a low melting point, liquation from the gangue is a very simple operation; it is, however, by no means so easy as it would appear. The temperature must be very carefully regulated, as if too high—*i.e.*, much above a red heat—the melting point of Sb_2S_3, the sulphide is volatilized, and the product has not the dark iron grey colour required in commerce, but a red tint, and is difficult to sell. On the other hand, if too low much sulphide remains in the residue. The best results are obtained when the ore is in coarse fragments about the size of walnuts or hazel nuts.

When the ore is disseminated through vienstuff, and also contains oxide, as in some "smalls," it cannot be liquated in the ordinary way, as a more or less pasty mass is then obtained, owing to the formation of antimony glass, the fusible compound of Sb_2S_3 with Sb_4O_6, already described.

In such cases the ore should be mixed with some coarsely ground charcoal, placed in the liquation pot, and covered with more charcoal. The cover of the pot should be luted on. On heating, a satisfactory liquation will result. All smalls, if rich enough, can be treated in this way.

Access of air must be prevented as much as possible, whatever form of liquation apparatus or furnace is used, otherwise volatile Sb_4O_6 will be formed, and the loss of antimony will be excessive.

The process is carried on in :—

1. Pots.
2. Tubes.
3. Reverberatory furnaces.

The choice of one or other of these methods depends on local conditions, especially the cost of fuel and labour.

Liquation in Pots.—The pots are of various forms, but essentially they are fire-clay vessels, generally more or less crucible-shaped, with perforated bottoms and closely fitting covers. The receivers are also of fire-clay, and generally of the form of ordinary crucibles.

In Hungary the furnace, pots, and receivers were of the forms and arrangement shown in Fig. 205. The pots are set in a row on each side of the fire. The receivers which are placed outside the furnace are connected with the pots by a clay pipe. They are emptied only after two or three or more charges have been worked.

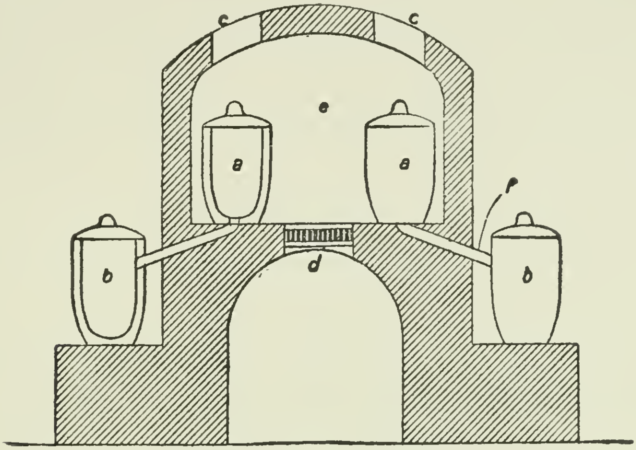
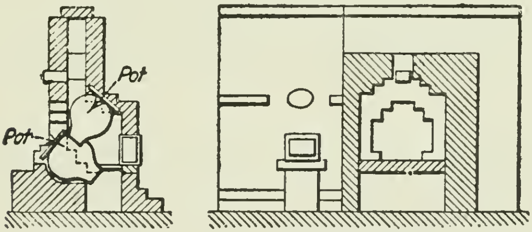


Fig. 205.—Liquation in Pots.*



CROSSECTION

CHARGING SIDE

Fig. 205*a*.—Section of Liquation Pot and Furnace, China

One disadvantage of this arrangement is the tendency of the liquated sulphide to solidify in the receiver, and to avoid this, in some works, the receivers are placed in recesses immediately below the pots, the latter then being set on a perforated fire-clay tile. The recesses should be provided with doors which can be closed, so that the receivers may be kept hot. The capacity of the pots varies from about 35 to 75 lbs.

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* Wang, *The Metallurgy of Antimony*, p. 72.

In a properly constructed furnace of this type there is a greater yield of sulphide and less loss of antimony by volatilization than in the tube furnace described below, but the process is intermittent, and entails much labour and a large consumption of fuel.

Liquation as practised in China and as I have seen it carried out in Japan is conducted as follows:—The furnace and pots used in Japan are shown in Fig. 205*a*.[*] There are two pots in each furnace. The pots are made of fire-clay. The upper, which will hold a charge of about 50 lbs. of ore, is perforated in the bottom with one or two $\frac{1}{2}$-inch holes, through which the liquated sulphide trickles into the lower or collecting pot. When sufficient molten sulphide has accumulated in the lower pot it is laded out into iron moulds. The lower pot is embedded in the ashes, so as to avoid the full temperature of the furnace.

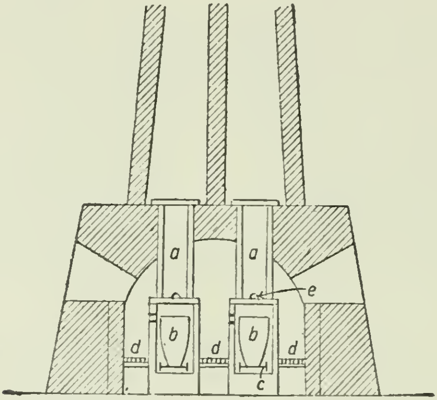

Fig. 206.—Liquation in Tubes.

The tube furnaces which were in use at Malbosc (France) have been given up and been replaced by the Herrenschmidt apparatus described on p. 579.

One of the old furnaces is shown diagrammatically in Fig. 206.[†] The tubes, of which there are four in each furnace, are set on fire-clay tiles perforated with holes, through which the liquated sulphide runs into the receivers in the vault below, each receiver being carried by an iron bogie *c*. There are three fire-places by which the tubes are heated. The receivers *b b* are also heated by part of the flames passing through openings in the sides of the vault, so that the liquated sulphide is kept molten. The charge is introduced at the top of the tube, the cover being temporarily removed, and the residues are raked out through the opening *e*, at the bottom of one side, which is closed during working with a fire-clay slab carefully luted. Each tube takes

[*] *Eng. and Min. Journ.*, Oct. 1917, p. 684.
[†] Wang, *The Metallurgy of Antimony*, p. 74.

a charge of about 4 to 5 cwts. of ore. This requires about three hours for liquation.

The disadvantages of the process are—greater loss by volatilization than when pots are employed, and only half the sulphide contained in the ore is obtained, but the cost of labour and fuel is low, and the process is a continuous one.

Liquation in reverberatory furnaces is practised in a few works, but the operation is attended with considerable difficulties. One of the chief drawbacks is the impossibility of keeping a reducing atmosphere in the furnace chamber, thus an excess of air is nearly always present, with the result that Sb_4O_6 is liable to be formed which volatilizes, and Sb_2O_4, which does not liquate. Further, the temperature is difficult to regulate.

The furnace usually employed for liquation is a reverberatory furnace of the ordinary type, but with a deep bed and a taphole at one side. A more efficient furnace, however, is one of those used in the liquation of tin; but whatever form of furnace is employed the loss of antimony by volatilization is excessive, unless an efficient condensing plant is provided, and the residue will often contain from 10 to 15 per cent. of the metal. The advantages of this method are large capacity, low cost of fuel, labour, and repairs.

The liquated sulphide or crude antimony is sent to market in the form of ingots, which should possess the following characters, viz. :—

They should be of a bluish tint without any trace of redness, and when fractured should show a well-marked radiated structure. The impurities present are iron sulphide always, and occasionally lead and arsenic sulphides, the last two being especially deleterious. The percentage of Sb varies from 68 to 73, and it is usually sold as 70 per cent. standard.

The following analyses * of Chinese crude antimony are by Schoeller, who points out that the Sb present is in excess of the theoretical amount (71·45) required by the formula Sb_2S_3. This he attributes to the presence of antimonious oxide and a small amount of metallic antimony :—

CHINESE CRUDE ANTIMONY.

	1.	2.	3.
Sb,	71·60	71·70	73·56
As,	0·06	0·048	..
Fe,	0·821	0·14	0·70
Cu,	0·015	not determined	..
Pb,	0·011		..
Zn,	0·071	0·22	..
Insol.,	0·408	0·24	..
S,	21·60	24·92	22·45
O,	not	determined	3·18
	94·586	97·268	99·89

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* *Journ. Soc. Chem. Ind.*, 1913, p. 261; *ibid.*, 1914, p. 169.

II. *Treatment of Rich Stibnite or of the Liquated Sulphide for the Production of Metallic Antimony.*—The method adopted is known as the "precipitation" method; also as the "iron-reduction" method, as it depends on the decomposition of antimony sulphide by iron.

$$Sb_2S_3 + 3Fe = Sb_2 + 3FeS.$$

It is only suitable for rich ores and the liquated sulphide (crude antimony).

The operations may be carried out either in crucibles or reverberatory furnaces. When the former are employed the process is known as the English process, the latter are, however, also in use in English works.

The Precipitation Process using Crucibles.—According to E. Rodger,* the process, as conducted in crucibles in the works in which he was engaged, was as follows:—

The ores for smelting by this process must be free from lead and arsenic, as these metals are not eliminated. The operations are conducted entirely in crucibles 20 inches high and 11 inches in diameter, made of a mixture of fire-clay and plumbago. The furnace, in which they are heated during the various fusions, is a reverberatory with a bed 54 feet long, including the fire-places, and 7 feet 4 inches broad, covered by a low arch, which springs almost from the surface of the ground, the bed being below the ground level. There are two fire-places, one at each end, drawing into a common flue in the middle of the bed of the furnace. The roof is covered with iron plates, and rises so little above the ground that it can be easily stepped on by the workmen during the operations. The crucibles are lowered into their places through circular holes in the roof, of which there are forty-two—*i.e.*, twenty-one on each side.

The ore or liquated sulphide is ground and passed through a coarse screen, so that the largest pieces are of the size of hazel nuts. After screening, a sample is assayed to determine the amount of iron required for the proper reduction of the sulphide.

In ordinary practice the process consists of three stages.

Stage 1.—Reduction of the sulphide. The charge for each crucible for a 52 per cent. ore consists of—

42 lbs. ore.
16 lbs. wrought-iron scrap, preferably tinned plate scrap.
4 lbs. common salt.
1 lb. slag from stage 2.

Part of the iron scrap, about 13 lbs., is beaten up into a ball, the remainder being added in the form of turnings or borings mixed with the ore and salt. The crucibles being already in the furnace, the mixture of ore, salt, and iron is charged in through an iron funnel, the ball of scrap being thrown in last. The furnace is then closed.

As the charge melts, the ball of scrap is gradually absorbed, the iron reducing the antimony sulphide to metal, and being itself converted into ferrous sulphide in accordance with the above equation. The salt assists the separation of the slag, and tends to promote the fusion of the gangue of the ore. During the operation each crucible is examined from time to time, and when necessary the ball of scrap is pressed down with a bar of iron. The length of time required for fusion and reduction depends on the position of the crucible in the furnace, but as a rule four meltings are got from each crucible per twelve hours.

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* *Journ. Soc. Chem. Ind.*, vol. xi., pp. 16 to 19.

Opposite the furnace opening above each crucible employed for reduction, is placed a cast-iron mould, capable of holding the whole of the reduced metal and slag, and furnished with an iron lid. The contents of the crucible when the fusion is complete are poured into this mould, which is at once covered with the iron lid, and the crucible is returned to the furnace. When cold the slag is knocked from off the ingot of metal, and is generally sufficiently poor to be thrown away.

The metal produced is known as "singles," and has the following approximate composition :—

Sb,	91·63
Fe,	7·23
S,	0·82

The high percentage of iron arises from the excess of iron which must be used to effect the proper reduction of the sulphide, and the next operation has for its object the removal of this iron.

Stage 2.—The charge for this fusion consists of—

84 lbs. "singles" broken to about the size of road metal.
7 to 8 lbs. liquated sulphide.
4 lbs. common salt.

The fusion is closely watched, great care being taken that the metal and sulphide shall mix thoroughly. Stirring with iron tools must, however, be avoided, as far as possible, as the object of this stage is the removal of iron. When the charge is completely fused, the slag is carefully skimmed off to leave the metal perfectly clean. The metal is then poured into moulds precisely similar to those used in stage 1. The metal is known as "star bowls," and a sample analyzed consisted of—

Sb,	99·53
Fe,	0·18
S,	0·16

(Generally, however, this metal is more impure, and contains especially a larger percentage of sulphur.—W.G.)

The slag contains antimony, and goes to stage 1.

The reaction which occurs in this fusion is similar to that in stage 1, the iron in the "singles" unites with the sulphur of the sulphide, iron sulphide and metallic antimony being formed.

As in stage 1, it was necessary to add an excess of iron to reduce and remove all the antimony from the ore, so in this stage it is necessary to add an excess of antimony sulphide to react with and remove all the iron, hence the presence of sulphur in the metal obtained.

In order to remove this sulphur and purify the metal another melting is required.

Stage 3—"Starring."—The object of this fusion is not only to remove the sulphur, but to obtain the antimony in the form required by the market—viz., flat cakes or discs, each bearing the "star" or fern leaf crystallization on the upper surface, by means of which buyers judge of the quality of the metal (see p. 563). These two results are achieved by fusing the "star bowls" with a flux known as "antimony flux," prepared by melting together American potash (commercial potassium carbonate) and liquated antimony sulphide in proper proportions, usually 3 parts of the former to 2 parts of the latter.

The "star bowls," after having been completely cleaned from slag, and this is absolutely necessary, are broken into small pieces, and charged into the crucibles.

The charge used is 84 lbs. of star bowls for which about 8 lbs. or more of antimony flux will be required, according to the size of the cakes or ingots, as it is essential that the flux should completely cover and surround them.

The crucibles are carefully watched, and when the metal begins to melt the flux is added. As soon as the fusion appears to be complete the charge is stirred once round with an iron rod, and immediately poured into iron moulds. As stated above, the ingots or cakes must be completely surrounded by flux. There must be a thin layer of it between the mould and the metal, and the entire surface of the ingot must be covered to the depth of about $\frac{1}{4}$ inch, otherwise a good "star" will not be produced. A considerable amount of volatilization takes place during the operations, to the extent of about 10 per cent. of the antimony, and to condense and collect it suitable flues and condensing chambers must be provided. The process has several disadvantages, notably the high cost of labour, fuel, and crucibles, and the small scale of the operations, but the loss of antimony is less than when reverberatory furnaces are employed.

The Precipitation Process using Reverberatory Furnaces.—One of the difficulties attending the precipitation process, especially when reverberatory furnaces are employed, arises from the little difference which exists between the specific gravities of antimony and ferrous sulphide, their separation hence is not so perfect as could be desired.

To overcome this, as far as possible, fluxes, such as soda ash, salt cake (sodium sulphate), and common salt are added to the charge. The salt cake, which becomes sodium sulphide by the action of the carbon present, is specially valuable, as it forms a fusible slag of comparatively low specific gravity with the ferrous sulphide.

The furnaces employed in most European works are of rather antiquated construction, and not well adapted for the operations. In the author's opinion a small copper smelting reverberatory furnace with a deep bed sloping to a taphole in one side would be the most efficient furnace for the process.

Tapping should be adopted, and not lading. According to G. Pautrat,* the process is being worked successfully at a smelter in Mayenne (France). The ore treated contains 50 to 60 per cent. Sb.

The process is carried on in two stages, viz. :—

1. Fusion with scrap iron to produce crude metal.
2. Refining fusion yielding metal with only 0·5 to 0·8 per cent. of impurities.

Stage 1—*Reduction Fusion.*—The reverberatory furnace used in the first stage has a bed about 10 feet long by 4 feet broad, with a large fire-place at one end, and two small dust chambers about 4 feet wide and 6 feet high at the other. The utility of these chambers is questionable, as the temperature prevailing in them is too high for the condensation of any oxide. The furnace having been heated, the process is begun by charging in a mixture of fusible slags and sodium carbonate followed by a charge of rich ore also mixed with sodium carbonate. The temperature is then raised until complete fusion takes place, the contents of the furnace being well mixed by rabbling. The siliceous and other impurities of the ore form a slag which is skimmed off and thrown away.

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* *Eng. and Min. Journ.*, vol. lxxxiv. (1907), p. 493.

As soon as the surface of the bath has been thus cleared, scrap iron, usually in the form of detinned cans free from solder, is added and rabbled in, the temperature being again raised. Decomposition of the antimony sulphide ensues, and the metallic antimony settles beneath the slag of ferrous sulphide and fused alkali. Another charge of ore and scrap iron is added, and the operation is repeated until the level of the bath reaches the working door in the side of the furnace. The iron sulphide is then laded into iron pots, care being taken not to dip the ladle in too deeply.

The metallic antimony is laded out in the same way, and cast into ingots or cakes, about 660 to 770 lbs. of metal being removed each time—*i.e.*, every three hours. This corresponds to a charge of the following weights and composition :—

Rich ore (50 to 60 per cent. Sb), ...	992 lbs.
Washed ore fines (about 45 per cent. Sb), . .	330 „
Slag from second or refining fusion (about 20 per cent. Sb), ...	44 „
Sodium carbonate, ...	44 „
Scrap iron, ...	529 „

If the operations have been carefully carried out the coarse antimony will not contain more than from 1 to 2 per cent. of iron, otherwise as much as 5 per cent. may be present. A representative sample was composed, as follows :—

Sb, ...	94·42
S, ...	1·95
Fe, ...	2·75
Pb, ...	0·22
As, ...	0·54

Both the waste products of the operations contain antimony, the slags 1 to 2 per cent., and the iron sulphide occasionally 10 to 12 per cent., the average being 6 to 7 per cent. In the latter the antimony occurs as sulphide, and as globules of metal when the temperature of the furnace has been too low to permit a clean separation.

The process thus far is almost identical with that of Sanderson.*

Stage 2—*Refining Fusion.*—The refining operation is carried out in a furnace like that for reduction but smaller. The impure antimony is remelted, taking care to prevent oxidation by covering the metal with a thin layer of fusible slag composed mainly of sodium carbonate. The molten bath is kept for a while at a brisk heat, to allow the impurities to rise to the surface, when they are skimmed off. A mixture of antimony oxide, oxysulphides, sodium carbonate, and a little coal is then thrown in in sufficient quantity to cover the metal. The progress of the refining is ascertained by taking out small quantities of the metal from time to time, casting it in ingots covered with slag, and noting the appearance of the surface, the end being denoted by the formation of the " star " or fern-leaf crystallization. The antimony is then laded out and cast into ingots, weighing about 45 lbs. A portion of the slag which covers the metal in the furnace is previously introduced into the mould, so that it may completely envelop the ingot, and thus allow it to solidify slowly in order that the " star " may be formed. The composition of the antimony obtained is given on p. 563.

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* See *Min. Ind.*, 1902, p. 43.

The production of refined antimony by this process is about 80 per cent. of that contained in the ore.

III. *Blast-furnace Smelting of Stibnite.*—A paper read before the Institution of Mining and Metallurgy * by Dr. W. R. Schoeller, who has had considerable experience in the treatment of antimony ores, is a valuable contribution to the metallurgy of the metal.

" In his opinion ores containing about 25 to 40 per cent. of metal, while no longer suitable for roasting, are yet too poor for liquation or direct precipitation processes. For these, as well as for by-products of the same richness, the blast furnace is undoubtedly the best appliance. Its advantages are, its large capacity, and the ease with which all kinds of by-products, foul slags, furnace bottoms, and residues can be worked up, giving metal, high-grade fume, and a final slag practically free from metal."

In repeated trials in smelting an ore containing 49 to 57 per cent. Sb in a gangue chiefly quartz in a blast furnace 36 inches in diameter, using a ferruginous slag from a lead-smelting furnace and lime as fluxes, he obtained the following results :—At first he used an excess of the ferruginous slag and 15 per cent. coke. The result being that much iron was reduced, and the antimony obtained was largely alloyed with that metal. On reducing the quantity of this slag to the amount only necessary for the fluxing of the gangue of the ore, and also diminishing the volume of the blast, no iron was reduced, and antimony of a high degree of purity as regards freedom of iron was obtained, though it was contaminated with lead from the slag from the lead blast furnace.

He, therefore, recommends smelting in a blast furnace as the best method for the treatment of stibnite ores containing 25 to 40 per cent. Sb. The following conditions to be observed :—

The charge to contain not more than 20 per cent. Sb.

The smelting column to be over 15 feet.

The amount of ferruginous material not to be more than sufficient to flux the gangue of the ore.

The amount of coke to be less than 10 per cent.

The pressure of the blast to be reduced to a minimum consistent with efficient smelting.

The slag and metal to run continuously into a small reverberatory furnace heated by its own fire for their separation.

A complete condensing system for the collection of the fume. This might be a dust chamber with long iron flue for cooling, and finally a bag-house, or a wet condensing tower, as used in the Chatillon and Herrenschmidt process.

As to the theory of the process, Dr. Schoeller's earlier researches,† together with the operation described, have convinced him that the blast, and the blast only, is responsible for the production of the antimony; and that this mode of smelting is a purely oxidizing process in which the metal is formed in two stages which proceed simultaneously: first, the molten stibnite absorbs oxygen from the blast, giving trioxide which is soluble in the sulphide; secondly, the oxide at once reacts with a further quantity of sulphide with formation of metal and SO_2, thus:—

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* *Trans. Inst. Min. and Met.*, 1918, p. 237. † *Journ. Soc. Chem. Ind.*, 1915, p. 6.

(1) $2Sb_2S_3 + 9O_2 = Sb_4O_6 + 6SO_2$. (2) $Sb_4O_6 + Sb_2S_3 = 6Sb + 3SO_2$.

"A mixture of antimony sulphide and oxide evolves sulphur dioxide, and yields metal when heated in a current of inert gas, but does not do so when fused in a crucible under a layer of flux" (*Schoeller*).

IV. *Treatment of Antimony Ores by Roasting.*—The ores which are suitable for treatment by roasting are poor ores containing stibnite, or stibnite mixed with oxidized antimony compounds, and liquation residues. The product of roasting stibnite will be either Sb_2O_4 or Sb_4O_6, according to the conditions under which the operation is performed, the former being non-volatile and the latter volatile. When the object is to produce the volatile oxide, the operation is termed "volatilizing-roasting," and is carried on under the conditions and in the manner described on p. 576.

Simple Roasting—i.e., roasting for the production of the stable tetroxide.—When stibnite (antimony trisulphide) is roasted with excess of air at a temperature of about 350° C. Sb_4O_6 is produced, of which a part is oxidized to Sb_2O_5. The Sb_2O_5 unites with some of the Sb_4O_6, forming the tetroxide (Sb_2O_4). If the ore contains any sulphides or oxides of foreign metals antimonates of these metals are formed. The roasting of stibnite is one of the most troublesome and difficult metallurgical operations, because its success requires a most painstaking attention to the maintenance of the right temperature in the furnace. The proper temperature is about 350° C.; if it is too low the roasting is incomplete, the sulphide only being partially oxidized, and very fusible antimony glass is formed by the union of the trioxide and sulphide. On the other hand, if it is too high the ore frits and balls together, and access of air to the interior of the lumps is prevented, volatilization of antimony as Sb_2S_3 and Sb_4O_6 also takes place.

The tendency to balling is lessened when there is much gangue present in the ore. Rich sulphides are the most difficult to roast, and require constant rabbling to prevent agglomeration.

The furnaces employed in the process are of many kinds, but there are none better than the ordinary hand-worked reverberatory roaster (see p. 23) of suitable size, and connected with one of the types of condensing plant, either that of Herrenschmidt (p. 579) or Chatillon (p. 578). The dimensions of the hearths of those in use range from 40 feet by 7 feet 6 inches to 26 feet by 6 feet 6 inches; whilst in some they are only 10 feet by 6 feet 6 inches.

The long furnaces have great advantages over the others, as the fire can be kept uniform and the ore is brought gradually to the hottest part near the fire-bridge, which it only reaches after it has been well oxidized; any tendency to agglomeration and volatilization is thus diminished. The work, too, is continuous, and not intermittent, as in the short furnaces.

The operation is a tedious one, and usually not more than 20 to 25 cwts. can be roasted in twenty-four hours, whilst the product is never only tetroxide on account of the impurities in the ore, and the irregularity, which cannot always be avoided in the roasting. It generally contains varying amounts of antimony glass, undecomposed sulphide, antimonates, arsenates, and sulphates of foreign metals.

The loss of antimony is said to be from 5 to 8 per cent.

If insufficient air is admitted during the operation Sb_4O_6 will be formed, and the loss be greatly increased.

The ore, after being roasted, as described above, is reduced to antimony regulus (metallic antimony) in the same manner as the trioxide obtained by volatilizing-roasting, p. 581.

It has been proposed to use the Huntington-Heberlein pot roasting process for the roasting of stibnite, but it has not yet been adopted in actual practice.

Treatment of Ores by the Process of Volatilizing-Roasting.—The process of volatilizing-roasting depends on the property possessed by antimony trisulphide, when heated to the necessary temperature with a limited supply of air, of yielding volatile antimony trioxide which can be condensed and collected in suitable apparatus.

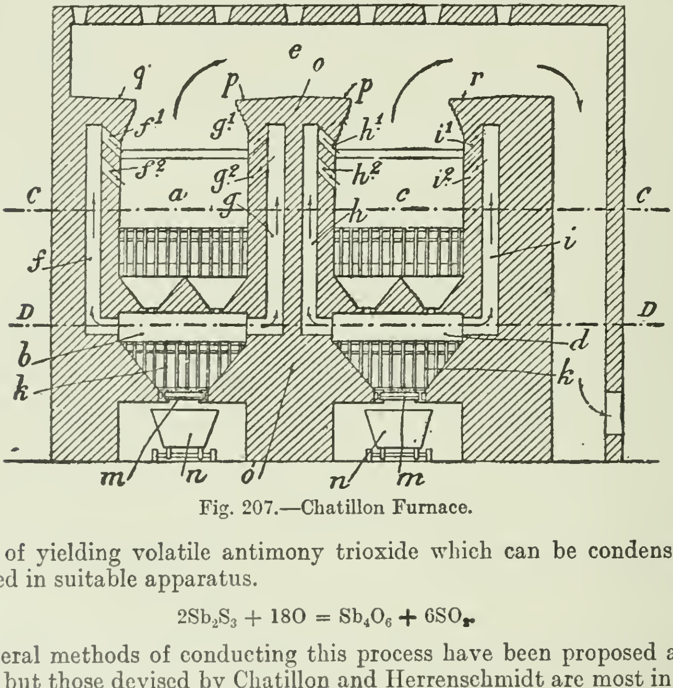

Fig. 207.—Chatillon Furnace.

$$2Sb_2S_3 + 18O = Sb_4O_6 + 6SO_2$$

Several methods of conducting this process have been proposed and are in use, but those devised by Chatillon and Herrenschmidt are most in favour in France, where the process is chiefly employed. The Herrenschmidt process is also in use in Yunnan and Hunan (China).

The advantages which are claimed for the process are :—

1. The separation of arsenic from antimony owing to the greater volatility of As_2O_6 as compared with Sb_4O_6.
2. Low-grade ores containing from 7 to 20 per cent. of antimony can be profitably treated.
3. The loss of antimony is low.
4. The consumption of fuel is low.

5. A large proportion of the gold and silver when present in the ore will be found in the residue.

6. The Sb_4O_6 produced can be either reduced to metallic antimony or can be used for the manufacture of pigments, etc.

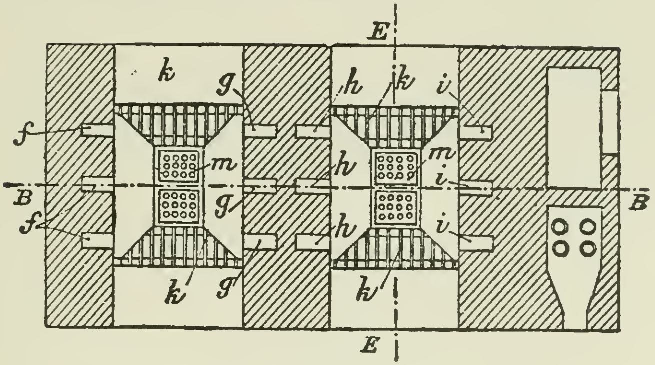

Fig. 208.—Chatillon Furnace.

Mons. E. Chatillon, of Brionde (France), is said to have been the pioneer and inventor of the sublimation method as applied to the treatment of low-grade ores, but this is disputed by Herrenschmidt.

The Chatillon Process.—A description of the process and plant, of which the following is a summary, is given by the inventor in the *Mining Journal* of 22nd August, 1908:—

The volatilizing-roasting of the ore is conducted in a furnace composed of two double cupolas *a*, *b*, *c*, *d*, Figs. 207, 208, and 209,* rectangular in cross-section, and arranged as shown. The two upper furnaces open into a chamber or flue *e*, which is common to both, and terminates in the downtake through which the fumes are led to the condensing plant.

The upper part of the wall dividing the two cupolas projects on each side, so as to form a kind of platform for receiving the ore charged in. The upper parts of the other sides of the cupolas similarly project for the same purpose. Within the walls of the upper cupolas are vertical flues which communicate with the lower cupolas.

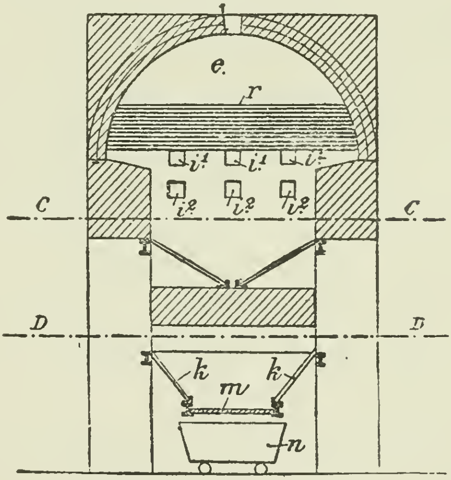

Fig. 209.—Chatillon Furnace.

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* Wang, *op. cit.*, pp. 96, 97.

Each of the lower cupolas *b* and *d* is fitted on two sides with inclined bars forming grates, the other sides being of fire-brick, thus forming a kind of hopper. The bottom is closed by a plate of thick perforated sheet iron, on opening which the spent residue drops into the truck below. The function of the lower cupolas is to receive the cinder from the upper cupolas, to complete the oxidation of any undecomposed sulphide and the extraction of the Sb_4O_6, and at the same time to cool the cinder and preheat the air supplied to the upper cupola through the vertical flues *f*, *g*, *h*, *i*.

The condensing system consists of sheet-iron tanks, through which water is circulated. The tanks are contained in chambers divided into compartments, with a tank in each compartment, the whole being arranged so as to compel the gases to circulate over the entire surface of the tanks, and thus cool them completely. At the exit from these chambers are placed one or more fans, which draw the gases through the system and force them either through a series of iron pipes for further cooling when necessary, or directly into a filtration chamber or bag-house. The bags are of coarse cotton canvas, or better, of woollen material, about 1 foot 8 inches to 2 feet in diameter and 26 to 36 feet in length. They are hung and arranged in exactly the same manner as in the bag-house for the collection of zinc white (see p. 502).

The main features of the process are :—

1. The possibility of treating ore fines.
2. Utilization of part of the heat of the gases.
3. Filtration of the gases in a bag-house.

The Chatillon process is conducted as follows :—Each furnace is charged with ore and fuel, coke, or charcoal, in alternate layers. Coke is preferred as fuel, but charcoal can be used.

The ore, which may be in the form of lumps or dust, when charged in falls upon the platform or hearth *p p*. Here the antimony sulphide liquates out and falls in drops, half into one cupola and half into the other, passing in its fall through the hot air from the lower cupolas which enters the upper cupolas at f^1, f^2, g^1, g^2, and h^1, h^2, i^1, i^2. The sulphide is thus oxidized and volatilized as Sb_4O_6. After the sulphide has liquated out the residue is pushed into the cupolas to complete the extraction.

The gases from the cupolas are drawn by fans into the cooling and condensing chambers, but before entering these chambers their heat is utilized for various purposes, such as heating furnaces, in which ore is liquated for the production of crude antimony, or in which oxides are reduced to metallic antimony, also for drying small ore or other materials, and for several other purposes.

The gases then traverse the chambers, in which they are cooled by passing over the surface of water circulating in tanks, and enter the fans. If any further cooling is necessary, they are forced by the fans into a series of iron pipes, generally water-cooled, and thence into the bag-house, otherwise they are forced direct into the bag-house. Before entering the bag-house the temperature of the gases must be reduced to about 100° C., lest they injure the material of the bags. The spent residue is removed by opening the iron plate at the bottom of the lower cupolas, when it falls into the truck below it. The oxide obtained is said to contain from 98 to 99 per cent. Sb_4O_6.

The Herrenschmidt Process.—The plant (Fig. 210) employed for this process comprises a furnace in which the oxidizing roasting is carried out

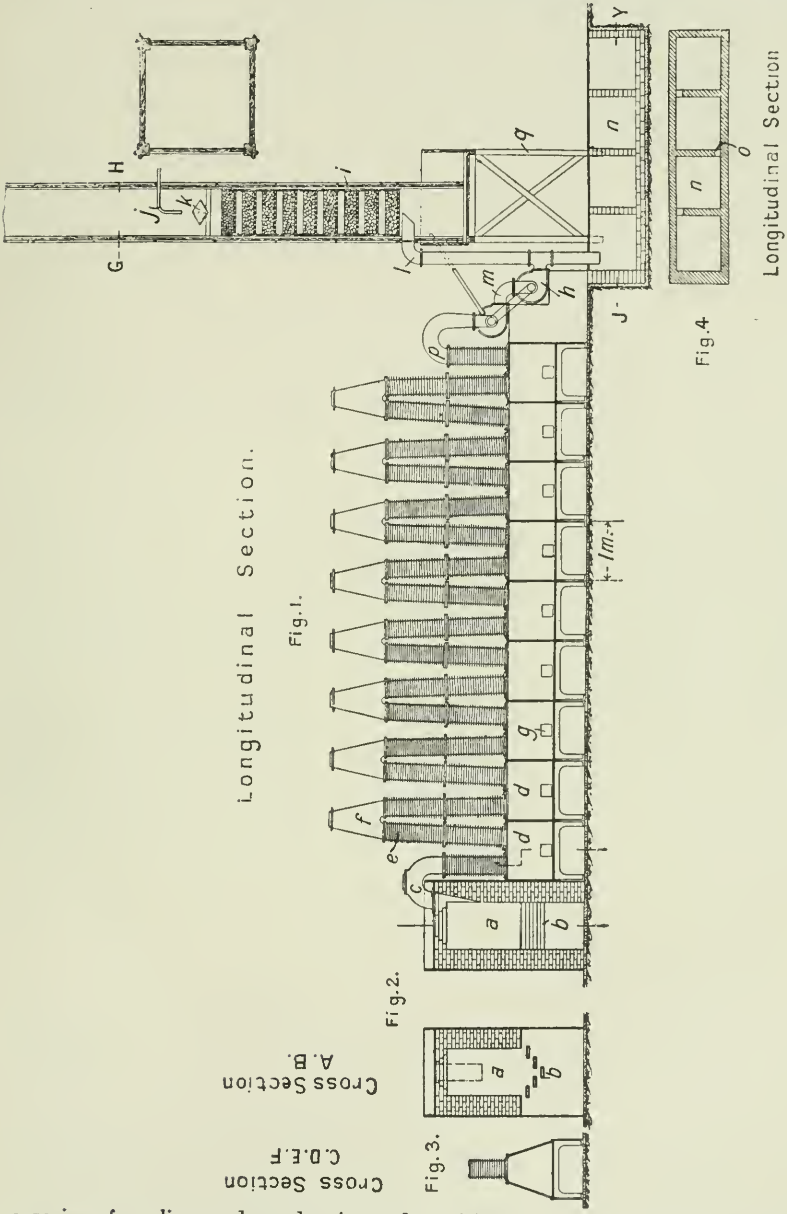
Longitudinal Section.
Fig.1.
Fig.2.
Cross Section A.B.
Fig.3.
Cross Section C.D.E.F
Fig.4
Longitudinal Section J.Y.
G
H
Y
J
j
k
i
q
n
o
l
m
h
p
f
e
c
d
g
a
b
1m

Fig. 210.—Herrenschmidt Plant.

a series of cooling and condensing tubes of iron set over collecting chambers, one or more fans, and finally a coke tower.

The furnace *a* is a rectangular shaft of fire-brick with a step grate of iron bars *b*, arranged as shown, and with an opening on one side near the top, to which is fitted an iron pipe for conducting the gases to the condensing system.

The condensing apparatus consists of a series of vertical or slightly inclined tubes *e* constructed of corrugated iron, or of iron with projecting horizontal wings (*tuyaux à ailettes*), to give a large cooling surface. These tubes are fixed over cast-iron chambers *d d*, of which there are nine, as illustrated in the figure. At the end of these condensers are two fans, which draw the gases through the system, and force them into a wooden tower, in which coke or, in some cases, vessels of pottery are packed. At the top of the tower water is admitted through the pipe *j*, and is distributed by the small tilting vessel *k*. Below the tower is a settler *n*, built of brickwork, divided into four compartments by three partitions, to receive the water coming from the tower and allow any oxide it may contain to settle and be collected.

The process is conducted in the following manner :—

The broken ore, which should be from $\frac{1}{3}$ inch to $1\frac{1}{2}$ inches in size, and from which the dust and fine particles have been separated by sifting, is charged into the furnace mixed with the necessary amount of charcoal, or preferably coke. A 20 per cent. ore will require about 4 per cent. charcoal or somewhat less coke.

The dust and fines are briquetted before charging. The atmosphere in the furnace is not excessively oxidizing, owing to the carbon in the fuel, hence the antimony sulphide is oxidized to the trioxide, Sb_4O_6, and not to the tetroxide, Sb_2O_4. The trioxide volatilizes and passes out of the furnace together with the gases from the fuel through the tube *c* to the first condensing and collecting chamber. The oxide which collects in this chamber is generally contaminated with about 23 or more or less per cent. of impurities, chiefly dust from the ore and ashes of the fuel in the furnace.

From this chamber the gases traverse successively the other tubes and chambers in which the oxide is condensed and deposited in a pure form.

Finally, the gases enter the fans, and are forced into the coke tower, up which they pass through the interstices between the pieces of coke, or the earthenware vessels, meeting a shower of water from the water distributor above. The last portions of the oxide are thus condensed and washed out of the gases. The water from the tower runs into the settler below, where any oxide it may contain settles and is collected.

In the plant just described about $5\frac{1}{2}$ tons of ore, containing 20 per cent. of antimony, can be treated in twenty-four hours with a consumption of about 4 per cent. of charcoal.

The residue, as determined in two charges, contained about 1·3 per cent. antimony, and the total loss of antimony was about 10 per cent. of that in the ore. The different parts of the apparatus, however, were not thoroughly cleaned ; if they had been, the loss would probably not have exceeded 5 per cent.

" The guaranteed results of such an apparatus are that the yield in oxide will not be less than 90 per cent. of the metal contained in the ore. With ores coming directly from the mine, and containing 10 to 15 per cent. of antimony, 6 tons per twenty-four hours can be treated with a consumption of 4 to 5 per cent. of gas coke or 6 to 7 per cent. of charcoal. With ores containing 18 to

20 per cent. of antimony the capacity is 4½ tons per twenty-four hours, with a consumption of 5 to 6 per cent. of gas coke, or 7 to 8 per cent. of charcoal." [*]

V. *Reduction of the Antimony Oxides to Metallic Antimony.*—The products from the roasting operations, consisting of Sb_2O_4 from ordinary roasting, and Sb_4O_6 from the volatilizing-roasting process, are reduced to metal, generally in reverberatory furnaces, by carbon in the presence of alkaline fluxes. These fluxes are necessary, because, as has been pointed out (p. 562), when antimony tetroxide (Sb_2O_4) is heated with carbon alone it is only partly reduced to metal, and chiefly to Sb_4O_6, which volatilizes.

The fluxes generally employed are crude sodium carbonate (soda ash), sodium sulphate (salt cake), and sometimes common salt, the sulphate by the action of carbon becoming sodium sulphide. They give very fusible slags, which not only protect the metal, but also partially refine it The alkaline sulphide dissolves any antimony sulphide left in the oxides, and also converts the compounds of the foreign metals present into sulphides, so that they are removed in the slag, whilst the sodium carbonate fluxes the gangue.

The process is usually conducted in small reverberatory furnaces, but if the ores roasted for Sb_2O_4 are poor in antimony, or poor oxidized ores have to be treated, blast furnaces may be employed.

In France, where this process is employed on a more extensive scale than elsewhere, the roasted ore is treated together with Algerian oxide ores. The furnaces are small, having hearths of only about 8 feet by 5 feet or 10 feet by 6 feet. They only differ from ordinary reverberatories in the great depth of the hearth compared with its area. The hearth is of fire-brick, or of fire-brick covered with a working bottom of clay, and slopes towards a taphole in one of the long sides of the furnace, the working door being generally in the opposite side, but sometimes in front. Opposite the taphole there is a cast-iron pot for receiving the reduced metal. It is essential that the flue of the furnace should be connected with a condensing system of chambers or pipes, to collect any antimony that may be volatilized, and this is usually a considerable amount.

The composition of the charges varies with the richness of the roasted ore and the raw oxide ores, and the nature and amount of the impurities present. This is obvious when we consider that the former is not pure Sb_2O_4 but is always contaminated with the foreign matters mentioned on p. 565 A common charge, the weight of which will depend on the size of the furnace, consists of :—

Mixed roasted ore, and oxide ores, about . . .	100 parts.
Flux composed of soda ash, salt cake, and common salt, about	10 ,,
Hard charcoal, about	10 ,,
Foul slags, about	20 to 25 ,,

After the furnace has been heated to the proper temperature the charge is either thrown in and melted, or the fluxes are charged first and melted, the ores being added in small quantities from time to time. In either case the materials when fused are well mixed by rabbling. After the reactions are complete, the charge is allowed to settle, and the reduced metal and slag are tapped out into the pot in front of the furnace or into moulds. When they have solidified the slag is broken off, and the antimony, which is more or less impure, is sent on to the refining furnace. If arsenic, lead, or zinc have been present in the charge, they will be reduced to a greater or less extent during the process, and the antimony will be contaminated with them.

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[*] Wang, *op. cit.*, p. 98.

The reduction of the oxide Sb_4O_6 produced in the volatilizing-roasting process, and which may contain Sb_2O_4 and Sb_2O_5, is effected in the same manner as described above. The resulting metal is, however, usually fairly pure, and may be of the quality of " star " antimony. In that case it is received in crucibles containing " starring " flux, which has been prepared by melting sodium carbonate with antimony oxide and some sulphide in a separate furnace. The metal and flux are then poured into moulds. Sufficient flux to cover the metal during solidification must be used or the " star " will not be formed.

VI. *Refining Impure Antimony.*—The method of refining antimony in crucibles, which is chiefly in use in England, has already been described on p. 571. The metal is also refined in reverberatory furnaces. In France these furnaces are exclusively used in the most important works where the process is conducted in accordance with the best modern practice, as described on p. 573.

Extraction by Wet Methods.—As has already been stated, the extraction of antimony from its ores by means of solvents, although many methods have been experimented with, is not yet practised anywhere on a commercial scale.

The solvents which have been tried, and in some cases patented, may be mentioned ; they are hydrochloric acid, ferric chloride, sodium and calcium sulphides, and caustic soda.

Extraction by Electrolytic Methods.—Several of these methods have been proposed, but none has yet been adopted on a practical scale.

In the *Engineering and Mining Journal* * Mr. William A. Burr describes the working tests carried out by him at a small plant capable of producing 1,000 lbs. of electrolytic antimony daily. The ore treated was somewhat impure, containing 3 per cent. As and various percentages of other impurities.

The stibnite ore was crushed to pass an 8-mesh sieve in the solvent solution containing 7 per cent. sodium hydrate. The pulp was led away to two leaching tanks of Douglas fir, 16 feet in diameter, with 5 feet staves, and an ordinary filter bottom. The filter bottom was covered with one thickness of cocoa-matting covered with a seamless woollen filter cloth. When the leaching tank was filled, freshly standardized sodium hydrate solution was let in beneath the filter bottom and allowed to flow upward through the pulp and to overflow through launders as pregnant solution into the pregnant solution tank. Live steam was also introduced beneath the filter bottom, in order to maintain a working temperature of 60° C. From the pregnant solution tank, the solution was decanted into the precipitating cells. There were three cells, consisting of boxes of 2-inch Douglas fir, measuring 30 inches by 30 inches by 15 feet inside. Each cell contained 80 electrodes of mild steel $\frac{1}{8}$ inch thick and 2 feet square, placed 2 inches apart. The conductivity of the electrolyte was increased by the addition of 2 per cent. sodium chloride.

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* *Eng. and Min. Journ.*, Nov. 1917.

The most successful precipitation was accomplished under a tension of 2·25 to 2·50 volts and a current density of 8 to 9 ampères per square foot of cathode surface. This gave a coarse, crystalline precipitate, easily removable from the cathodes by means of a scraper. The precipitate was allowed to accumulate on the cathodes until a thickness of about $\frac{3}{4}$ inch had been deposited on both sides. It was then scraped off, washed, dried, and cast into the usual " star " antimony cake under a cover of melted resin or thin slag.

Its analysis showed 99·94 per cent. Sb.

ARSENIC.

Physical Properties.—Arsenic is a very brittle steel-grey metal with a brilliant lustre. It occurs in two forms—the crystalline and the amorphous. The former is in brilliant rhombohedral crystals, and is the form in which the metal is usually met with in commerce. It is obtained when the vaporized metal is condensed in a receiver at a temperature approaching that of the vapour itself. It does not readily oxidize in the air, and is hence preferred to the amorphous form.

The amorphous form is a dark-grey powder, which is produced when the temperature of the condenser is much higher than that of the volatilized metal, also when the vapour is diluted with other gases as H, CO, and CO_2. It readily oxidizes in the air, and is chiefly utilized in the manufacture of arsenical preparations.

Specific Gravity.—The crystalline variety has a specific gravity of 5·73, and the amorphous of 4·71.

Action of Heat.—Arsenic volatilizes at about 450° C., and its vapour has a strong odour of garlic. When heated, under ordinary circumstances, it passes directly from the solid state to the state of vapour, but when heated under pressure in a sealed tube it may be obtained in the fused state. The product, although brittle, may, however, be slightly flattened under a hammer.

Atomic Weight 74·96.

Chemical Properties.—The crystalline variety of arsenic undergoes no change in dry air at ordinary temperatures, but in moist air it undergoes oxidation. When heated in air it burns and is converted into As_4O_6.

Hydrochloric acid has but little action on it, but it is readily dissolved by nitric acid, *aqua regia*, and by a mixture of hydrochloric acid and potassium chlorate. It is also soluble in concentrated sulphuric acid, SO_2 being evolved.

When fused with sodium or potassium nitrates arsenates are formed.

There are two oxides—arsenic trioxide and arsenic oxide.

Arsenic Trioxide, As_4O_6 (Arsenious oxide).—Commercially known as "white arsenic." It occurs in two forms, the amorphous or glassy, and the crystalline. When newly prepared the amorphous form is transparent "arsenic glass," but when kept for some time it becomes converted into the crystalline form, when it is opaque.

Arsenic trioxide is slightly soluble in water, the amorphous being more soluble than the crystalline varieties. It volatilizes at about 200° C. When heated with charcoal it is reduced and metallic arsenic volatilizes.

"White arsenic" is the form in which arsenic is most widely used.

Its chief uses are in the manufacture of pigments, Paris green. etc., insecticides in agriculture, enamels, arsenic oxide, etc., and as a reducing agent in glass-making to remove the colour produced by iron oxides.

For its preparation, see p. 586.

Arsenic Oxide, As_2O_5, is prepared by the oxidation of As_4O_6 by nitric acid. Its sodium salt is in extensive use in calico printing.

Arsenic Sulphides.—There are three sulphides :—

Arsenic disulphide, As_2S_2. Found native as realgar.
„ trisulphide, As_2S_3. „ „ orpiment.
„ pentasulphide, As_2S_5.

None of these is of metallurgical importance

Alloys.—There are no alloys of arsenic, with other metals, of industrial importance; in very small amounts, however, its presence confers special properties. Thus metallic arsenic, or white arsenic with charcoal, is used in the manufacture of copper fire-box plates, which have to contain from 0·3 to 0·5 per cent. As, being added to the charge in the copper refining furnace (see p. 59).

It is also added in small quantities to the lead used in the manufacture of shot (see p. 179).

When arsenic is present in combination with Ni, Co, Pb, Fe, etc., it forms compounds, the speises, which have some affinity with mattes. They always contain silver and often gold.

TYPICAL SPEISES.*

	Ni Speise.	Ni-Fe-Pb Speise.	Cu-Pb Speise.
As, ...	34·07	20·10	12·98
Fe, ...	10·06	51·00	5·54
Pb, ...	..	10·10	26·11
Cu, ...	..	1·25	44·56
Ni, ...	52·58	14·90	0·71
Co, ...	3·28	..	1·63
S, ...	1·01	1·02	2·86
Ag, ...	..	0·05	0·13
Sb, ...	..	..	5·21

Ores of Arsenic.—They are very widely distributed in nature, but occur in comparatively few localities in sufficient abundance to be worked.

Native Arsenic.—Frequently contains gold and silver. In Upper Sarawak large masses occur with many ounces of gold per ton. It is generally found in association with ores of Ag, Pb, Co, and Ni, but is not an important source of arsenic.

Mispickel, FeS_2, $FeAs_2$ (Arsenical pyrites).—Contains 46·1 per cent. As. Part of the iron is sometimes replaced by cobalt. Frequently it contains gold and silver. At the Lucknow Goldfield, New South Wales, blocks of 2 to 5 tons assayed about 250 ozs. gold per ton, and other lumps of considerable size 1,500 to 3,000 ozs. per ton.† It is also associated with gold at Deloro, Canada. It is widely distributed, is the most important ore, and the chief source of arsenic. The principal deposits are in Germany, Cornwall and Devonshire, France, Spain, Portugal, and Canada. It occurs associated with ores of Ag, Ni, Co, Sn, Pb, and Cu.

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* Kerl, *Handbuch Metallurgischen Hüttenkunde,* pp. 759 to 761.

† *Trans. Inst. Min. and Met.,* vol. vii., p. 248.

Löllingite and Leucopyrite are iron arsenides, the former, $FeAs_2$, occurs massive, and the latter, Fe_3As_4, crystallized. They also often contain gold but only in small amounts.

Löllingite and Leucopyrite are important ores, but occur to a very much less extent than mispickel. The chief localities are Silesia, Styria, Bohemia, and Carinthia. The Silesian leucopyrite carries gold.

Realgar, As_2S_2, is mined in small quantities in Macedonia and in Persia.

Orpiment, As_2S_3, occurs in somewhat larger quantities, also in Macedonia, and in 1900 the production was about 500 tons.

The other minerals of arsenic are of no importance as ores, but the arsenide ores of cobalt and nickel afford a considerable quantity of arsenic in Saxony. Other sources of arsenic are tin and copper ores and metallurgical by-products, as flue dust, bag-house fume, and speises. The great bulk of the arsenic produced in the United States is obtained from flue dust. The chief producing countries in the order of their importance in 1909 were Germany, France, England, Spain, Portugal, Canada, and Mexico.

The Extraction of Arsenic.—Arsenic is extracted as metallic arsenic; white arsenic or arsenic trioxide; red sulphide of arsenic or realgar; and yellow sulphide of arsenic or orpiment.

Metallic Arsenic is prepared by heating mispickel or leucopyrite in fire-clay tubes, which are usually set in two rows in a gallery furnace resembling, but much smaller than, a Belgian zinc furnace. The tubes are about 2 feet 6 inches long and about 6 inches in diameter. Each tube is provided with a fire-clay condenser, and in the mouth of each is placed a spiral of sheet iron, which projects equally into both the tube and the condenser. At the beginning of the operation some arsenic sulphide sublimes, hence the condensers are not attached to the tubes until vapours of metallic arsenic are given off. In order to prevent or diminish the sublimation of sulphides, potash or freshly burnt lime is sometimes added to the charge.

On the hotter parts of the condensers, and on the iron spiral, the arsenic condenses in brilliant steel-grey crystals, while on the cooler parts, and if the arsenic vapour be mixed with other gases, it condenses as a dark grey easily oxidized powder, which is unfit for the market, and has to be used for making arsenical preparations. As soon as the furnace has cooled, the iron spiral is unwound, the crystals detached, and they are then ready for sale.

At Freiberg,* the richer mispickel, containing 35 per cent. As, was treated in twenty-six tubes in two rows in a gallery furnace.

A charge of 350 kil. yielded in eight to twelve hours 75 kil. metallic arsenic from the iron spiral, and 12 kil. of sulphides from the receivers.

The theoretical changes which occur in the process are :—

$$\begin{aligned} FeAs_2FeS_2 &= 2As + 2FeS. \\ 4FeAs_2 &= 7As + Fe_4As. \end{aligned}$$

In practice, however, much arsenic remains in the residue, which is generally worked up for As_4O_6.

Arsenious Oxide, White Arsenic, As_4O_6.—For the preparation of arsenious oxide, mispickel, leucopyrite, or arsenical ores of tin, copper, etc., are submitted to an oxidizing roasting when the As_4O_6 formed is volatilized and collected in flues and condensing chambers. The temperature should not be higher than is necessary to volatilize the arsenious oxide.

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* Stölzel, *Die Metallurgie,* p. 1526.

The furnaces employed are :—

Reverberatory Furnaces.—These have beds, 20 feet long and about 6 feet wide, built in pairs, so that the rabbling doors are only on one side of the bed. There are about five or six rabbling doors to each furnace, through which the ore which is fed through a hopper at the back is gradually worked by hand to the fire-bridge end.

The Brunton Calciner.—This furnace consists of a circular bed, from 12 to 16 feet in diameter, paved with fire-brick, which revolves slowly at from 5 to 10 revolutions per hour. The roof is of fire-brick. Above the bed, and built into the roof, are three cast-iron frames, in which are fixed the cast-iron rabbles. The rabbles are placed obliquely, so that, as the bed revolves, the ore which is fed at the centre is turned over and outwards till it reaches the periphery of the bed, when it falls into a chamber below. The heat is supplied from two furnaces on opposite sides of the bed.

Each furnace will roast 4 or 5 tons of ordinary ore per twenty-four hours.

The Oxland Calciner is an ordinary cylindrical roaster with continuous discharge. As used for roasting arsenical ores it is usually a wrought-iron cylinder, 25 to 30 feet long and about 5 feet diameter, lined with fire-brick, and having four longitudinal ribs. It is set at a slight inclination, and has a fire-place at the lower end. Its capacity is about 20 to 25 tons in twenty-four hours.

The flues in Cornwall and Devon are usually about 100 to 200 feet long, and then enter an extensive series of zig-zag flues or chambers, about 5 feet 6 inches high and 3 to 4 feet wide, and from these another long flue leads to a chamber with baffle walls, and then to the chimney stack.

The flues and condensing chambers are built of masonry or brickwork, and in some works in the cooler parts are constructed of sheet-lead, sometimes cooled by water. At the Gawton Mine, Tavistock, the flues are over 1 mile in length.

The crude arsenic, which will contain generally about 70 per cent. or more of As_4O_6, is taken from the flues and sent to the refinery.

Refining.—The crude arsenious oxide, which contains particles of ore, ash from the fuel, etc., is charged into reverberatory furnaces, similar to those just described, but of smaller dimensions, and resublimed. The fuel is a mixture of coke and anthracite, but gas-firing is best, as the sublimate must not be discoloured by smoke or soot. The vapours are led from the furnace, first through a hot flue, built of brickwork about 100 feet long, in which the flue dust and foreign matters settle, and then through a set of twelve zig-zag chambers, termed "kitchens," built in duplicate, so that, while one set is being emptied the other may be shut off. Each chamber is about 14 feet long by 4 feet wide and 7 feet high, and is built of brickwork. From the chambers the vapours pass into the main flue of the works, and thence to the chimney stack. The arsenious oxide condenses in the chambers in brilliant white crystals. After removal from the chambers, it is ground in a flour mill, and the ground product is packed in barrels for sale, each holding about 400 lbs., or it may be converted into white arsenic glass. Arsenious oxide, "white arsenic," is the form in which the great bulk of the arsenic extracted is produced.

At the Washoe Arsenic Plant, Anaconda, arsenious oxide is extracted from the flue dust from the main flue of the copper converter plant as follows:—The arsenic is derived from the enargite, Cu_3AsS_4, which is present in the ores smelted for copper. The finest portion of the flue dust, about 10 tons daily, yields from 3·3 to 5·5 per cent. As_4O_6.

The dust is roasted in a Brunton furnace, 14 feet in diameter, having thirty-three fixed rabble blades, and revolving ten times per hour.

The roasting is performed at a low heat, just visibly red (480° C.). The residue is discharged into hopper cars in a tunnel below.

The arsenic vapours pass into a flue, 240 feet long, 18 feet wide, and 7 feet high, with baffle walls every 7 feet. The crude arsenious oxide condenses as crystals on these and on the floor and sides. When sufficient has accumulated, the roasting is stopped, and it is removed for refining.

The crude product contains 85 per cent. As_4O_6, 4·3 per cent. Cu, 8·1 ozs. Ag per ton, and 0·025 oz. Au.

It is refined by heating it in a reverberatory furnace in 6-ton charges, when the volatilized As_4O_6 is condensed in a flue of the same dimensions as that described above. The crystalline product contains 99·8 per cent. As_4O_6. It is ground in Sturtevant mills, and packed in barrels for sale.

An important paper by Mr. J. O. Elton on the "Recovery of Arsenic Trioxide from Flue Dust," of which the following is an abstract, is published in the *Trans. of the American Institute of Mining Engineers*, vol. xlvi., pp. 690-702 *:—Arsenic trioxide is recovered from flue dust or fume by volatilization, the product obtained by a single roasting or distillation being classed as "crude arsenic." A second distillation gives a refined product often containing 99·97 per cent. As_4O_6. Muffle tests, in which time and temperature were varied, showed that below 649° C. the proportion of arsenic trioxide recovered is practically constant. Above this temperature lower yields are obtained owing to the formation of arsenates. Roasting with pyrites and powdered coke showed that when arsenic is once "burned in" (*i.e.*, converted into arsenates), it is not liberated again below about 870° C. The best results are obtained at 510° C., at which temperature arsenic pentoxide and pentasulphide break down and the trioxide is volatilized; only a small amount of sulphur trioxide is liberated, and the metallic oxides have a very low vapour pressure. The gas must be cooled to 121° C. to obtain complete condensation of the arsenic trioxide. The furnace should have a large capacity; large hearth area, with means for constantly shifting the surface of the dust; intimate contact of the hot gas with the dust, preferably a constant falling of the hot dust through a slow-moving current of the hot gas; continuous operation, with sealed feed and residue-discharge openings; gradually increasing temperature of the dust towards the residue-discharge end. The length of time the dust should remain in the furnace depends on the thickness of the bed of dust and the rabbling it receives; under favourable conditions, the arsenic trioxide is eliminated completely in 30 to 45 minutes. Rotating cylinder furnaces are suitable, preferably with a dust chamber at the end, from which the dust will slide back into the furnace. Multiple hearth furnaces make good first-refining furnaces. Cast-iron hearths give good transference of heat, and at 510° C. the rabble arms and castings do not need cooling

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* Abstract in *Journ. Soc. Chem. Ind.*, 1915, p. 362.

At the Deloro Gold Mine, Canada,* the ore, auriferous quartz, is largely impregnated with mispickel, which is also gold-bearing. The ore is crushed in a stamp mill, where about 60 per cent. of the gold is extracted by amalgamation. The tailing is concentrated on Wilfley tables and treated with cyanide and cyanogen bromide. The total extraction of the gold is about 90 per cent.

The concentrate contains about 30 per cent. As, and is roasted in two modified Oxland furnaces arranged in series. The first is 29 feet 6 inches by 5 feet 6 inches, and the second 60 feet by 6 feet 6 inches. The product of the first is delivered by a shoot to the second furnace below.

Nearly all the arsenious oxide is volatilized in the first furnace.

The fume from both furnaces is drawn mechanically through a dust chamber, 100 feet long, and then through zig-zag chambers, 12 feet wide, in which the white arsenic is deposited, and is then discharged into cars beneath the chambers. The product contains 85 per cent. As_4O_6. It is purified by resublimation in reverberatory furnaces in charges of 1,600 lbs. Ground white arsenic is the form in which arsenious oxide is most extensively used, but there is also a demand for the amorphous form, white arsenic glass.

White Arsenic Glass is fused arsenious oxide, and, when freshly prepared, resembles colourless plate glass in appearance, but, after a time, it becomes opaque from being changed into the crystalline form, and then appears white and porcellanous.

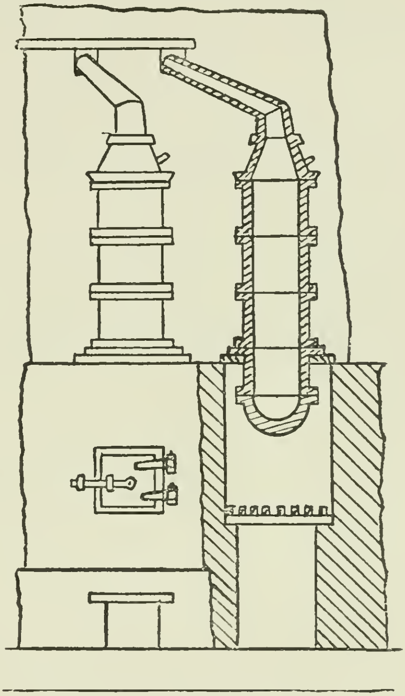

Fig. 211.—Sublimation Retort for Arsenic Glass.

It is obtained when the temperature of the receiver is such that the sublimed As_4O_6 is fused to a glass. If the temperature is too low much powdery crystalline sublimate is produced, while if it is too high much of the arsenious oxide will pass over into the condensation chambers beyond. In Saxony the sublimation is conducted in cast-iron pots, surmounted by three cylindrical condensers of cast or wrought iron, having on the top an iron hood terminating in a conical leaden top, from which a pipe leads to a condensing chamber (Fig. 211). The iron must not be highly graphitic, or some of the As_4O_6 will be reduced to metal, and the glass be discoloured.

The pots are 2 feet 5 inches deep and 23 inches wide, and each takes a charge of about 275 lbs. of white arsenic.

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* *Min. Ind.*, 1902, pp. 47, 48.

The three iron condensing cylinders are together 3 feet 2 inches high.

After the charge has been introduced, the fire is made up, and carefully regulated, so that the receivers are just hot enough to completely melt the condensed sublimate to glass.

At the end of the process the whole is allowed to cool, and the arsenic glass detached from the receivers with wooden hammers.

Formerly arsenic glass was manufactured at Hayle, Cornwall, by subliming white arsenic in shallow cast-iron pans with thick bottoms and collecting the fused glass on conical iron hoods, which were set over them. At present, however, but little is made in England.

Orpiment (Yellow arsenic glass).—The orpiment of commerce is prepared by subliming white arsenic with sulphur in various proportions, according to the colour required, and is really only arsenious oxide coloured by arsenic sulphide. The operation is carried out in the same apparatus as that used for white arsenic glass. At Freiberg from 2 to 4 kilos. of sulphur are placed at the bottom of the pan, and 125 kilos. of white arsenic upon it. The sublimed product condenses and fuses on the sides of the receivers, and only the sublimate which has fused is collected, the other being kept for resublimation with other charges.

Realgar (Red arsenic glass).—The realgar of commerce is artificial arsenic disulphide. It is prepared at Freiberg * by heating a mixture of mispickel and iron pyrites in fire-clay tubular retorts, resembling Belgian zinc retorts, but running right through the furnace, and collecting the sublimate in sheet-iron receivers. The retorts are about 4 feet 7 inches long by 6 inches in diameter, and twelve are set in each furnace in three rows. They are open at the charging end, and after charging the end is closed with a fire-clay tile luted in.

The mispickel and iron pyrites are mixed in such proportions that the sublimate "raw realgar" obtained may contain an excess of arsenic. The product will consist partly of fused and partly of pulverulent sublimate. The former is powdered and treated by the refining process, and the latter is resublimed.

The refining is necessary in order to obtain the desired colour, and this is effected by melting the raw realgar with sulphur in the proportions necessary for that purpose.

The pots employed are of cast iron, about 16 inches in diameter and 23 inches deep. The charge for each pot is about 330 lbs. raw realgar. This is melted with from 13 to 20 lbs. of sulphur with continual stirring. When finished the slag is skimmed off and the molten glass tapped off at the bottom of the pot into iron moulds. The product is ground for sale. It is used in pyrotechny to give a white light, and also in tanning.

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* *Preuss. Zeitschr.*, vol. xviii., p. 188.

BISMUTH.

Physical Properties.—Bismuth is one of the greyish-white metals, but possesses a characteristic reddish tinge. It has a highly crystalline structure, and when melted, allowed to cool slowly until the surface solidifies, the crust then broken, and the metal, which is still fluid, poured out, very large crystals may be obtained. They have the appearance of cubes, but are really obtuse rhombohedrons.

Malleability and Ductility.—Bismuth possesses neither of these properties, but is extremely brittle, its fracture being coarsely crystalline. It may be easily powdered.

Specific Gravity 9·80.

Action of Heat.—The melting point of bismuth is about 266° C., and at between 1,100° and 1,450° C. the metal volatilizes. It expands on solidifying.

Electrical Conductivity.—Very low, being only 1·13 if that of silver be taken as 100.

Atomic Weight 208·0.

Chemical Properties.—Bismuth undergoes practically no change in the air at ordinary temperatures, but when heated to redness it becomes coated with Bi_2O_3, and when molten is rapidly oxidized. It is soluble in nitric acid, *aqua regia*, and in hot concentrated sulphuric acid, the first two being the best solvents. Hydrochloric acid has no action on it when dilute, and even when concentrated and hot it dissolves it with difficulty.

Bismuth Oxides.—There are four oxides—viz., Bi_2O_2, Bi_2O_3, Bi_2O_4, and Bi_2O_5—Bi_2O_3 being of the chief importance.

Bismuth Trioxide, Bi_2O_3, is a yellow powder, which fuses readily to a reddish-brown fluid.

When silver containing bismuth is cupelled with lead, the lead is oxidized first, and the bismuth only towards the end of the operation. The bismuth then is oxidized to Bi_2O_3 in the form of the reddish-brown fluid just mentioned.

The salts which this oxide forms, when dissolved in acids, are decomposed by water, basic insoluble salts being formed, a property which is taken advantage of in the separation of bismuth from other metals.

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

$$Bi(NO_3)_3 + 2H_2O = (BiO)NO_3, H_2O + 2HNO_3.$$

Bismuth Trisulphide, Bi_2S_3, is found native as bismuth glance, or bismuthine. When roasted with access of air it is converted into a mixture of bismuth trioxide and bismuth trisulphate, $2Bi_2(SO_4)_3$, with evolution of SO_2, the sulphate being only partially decomposed on raising the temperature.

When molten it dissolves metallic bismuth in all proportions. It is soluble in nitric and in concentrated hydrochloric acid.

Commercial Bismuth.—The impurities present in the commercial metal are usually Pb, Cu, Ag, As, Sb, Fe, Au, and sometimes Ni, Tl, and Te. The following analyses show somewhat incompletely the composition of commercial refined bismuth :—

REFINED BISMUTH.*

	Saxony.	So-called Bismuth Purissimum.
Bi,	99·74 to 99·79,	99·85 to 99·98
Cu,	0·02 to 0·27,	0·016 to 0·032
Ag,	0·05 to 0·07,	..
S,	trace to 0·04,	..
Fe,	trace to 0·017,	trace
Pb,	0·084 to 0·11,	0·049 to 0·065
As,	trace to 0·011,	trace to 0·024

The amount of gold and silver in three samples of bismuth was found by E. A. Smith to be as follows :—

Australian bismuth,	Gold, 0·0110 per cent.	Silver, 0·3319 per cent.
German ,,	,, 0·0003 ,,	,, 0·0729 ,,
American ,,	,, 0·0005 ,,	,, 0·0705 ,,

The removal of the chief impurities is dealt with in p. 596. The chief uses of the metal are the preparation of alloys with low melting points, and of pharmaceutical products.

Bismuth-amalgam, with or without the addition of lead and tin, is occasionally used for silvering glass.

Alloys of Bismuth.—Bismuth forms alloys with many metals, with lead and tin, and with lead, tin, and cadmium, the so-called "fusible metals."

The composition and melting point of several of these alloys are given in the following table :—

"FUSIBLE METALS."

Name.	Bi.	Pb.	Sn.	Cd.	Melting Point.
Newton's metal,	8	5	3	0	94·5 °C.
Rose's metal,	2	1	1	0	93·75° C.
Lichtenberg's metal,	5	3	2	0	91·6° C.
Lipowitz' metal,	15	8	4	3	70·0° C.
Wood's metal,	4	2	1	1	60·5° C.

Bismuth also confers on its alloys the property of expanding considerably on cooling; they are, therefore, used for stereotype plates of the following composition :—

Lead 9, antimony 2, bismuth 2.
,, 10, ,, 1, ,, 1.

Also for casting delicate objects, and for taking impressions from dies, medals etc., the finest details being produced.

Bismuth and Lead.—These alloys are of no industrial importance.

If an alloy of lead and bismuth is cupelled, the lead oxidizes first and afterwards the bismuth. It is, therefore, possible to separate lead from bismuth by this means. The first portions of litharge formed will be free from bismuth, but as the lead is removed the litharge will gradually be more and more contaminated with it. The last portions will consist of litharge containing from 2 to 20 per cent. bismuth.

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* *Journ. f. Prakt. Chem.*, vol. xxiii., p. 75, and vol. xliv., pp. 23 to 48.

When lead containing bismuth is Pattinsonized the bismuth will be found in the enriched lead along with the silver.

Ores of Bismuth.—*Native Bismuth* is the most important source of the metal. It occurs largely in Bolivia, which is the chief producer of bismuth. It is also an important ore in Spain and Saxony, which come next to Bolivia as producers, and in New South Wales, Queensland, Bohemia, and Japan.

The native bismuth found at Schneeberg, Saxony, contains a small amount of arsenic, otherwise it is nearly pure. That from Sweden has the following compositions, according to analyses by Clive and Feilitzen :—

Bi,	95·16	91·15
Fe,	1·80	4·03
S,	1·42	2·28
SiO_2 (quartz),	0·23	0·34
Cu,	trace	trace

Bismuth Ochre, Bi_2O_3, generally occurs in the localities where native bismuth is found. In Bolivia it is also associated with bismuth carbonate, oxychloride, telluride, and sulphide.

Bismuth Glance, Bismuthine, Bi_2S_3, is found in all the localities mentioned above.

All the above ores occur in the localities given under native bismuth, also in smaller quantities in Styria, Carinthia and Mexico.

Bismuth also occurs in the ores of lead, copper, tin, cobalt, nickel, etc., and is frequently obtained from the by-products resulting from their treatment. Thus, for example, the litharge obtained in the cupellation of the rich lead from the Pattinson process, the residue from the Betts electrolytic process of refining lead and from the electrolytic refining of copper, and nickel and cobalt speise, are all sources of the metal.

The chief source of bismuth in America is the residue from the electrolytic refining of lead.

There is no record of the total amount obtained in the electrolytic refining of copper, but from 5 to 27 lbs. per ton of blister is recorded at some refineries.

The estimated export from Bolivia in 1926 was about 245 metric tons.

The production of bismuth is almost exclusively confined to the works of Johnson, Matthey & Co., London ; the Royal Smelters of Freiberg and Oberschlema, Saxony; and the Deutsche Gold-und-Silber Scheideanstalt, Frankfort.

The Extraction of Bismuth.—The extraction of bismuth is carried out by dry and by wet methods, and by a combination of both.

Dry Methods.—These methods are chiefly confined to the treatment of ores, the operations being performed in crucibles or reverberatory furnaces.

Wet Methods are employed for the extraction of the metal from metallurgical by-products, such as bismuthiferous litharge, liquors from the treatment of tin ores, and the slime produced in the electrolytic refining of lead and copper.

Dry Methods.—Formerly ores rich in native bismuth were treated by liquation in sloping iron tubular retorts of various forms, the temperature being such that the molten metal trickled away from the unfused gangue, and was collected in a pot or pots outside the furnace. This is not practised now, as ores sufficiently rich occur in but small quantities, and the residue left after liquation containing 5 or 6 per cent. of the metal had to be treated by other methods for its extraction. The ores to be treated may be :—

(*a*) Native bismuth with oxide.
(*b*) Oxide alone.
(*c*) Native bismuth with sulphide.
(*d*) Mixed oxide and sulphide with arsenides.

When large quantities have to be treated reverberatory furnaces are used, and in other cases crucibles.

On account of the volatility of the metal and its oxide, a comparatively low temperature must be employed, the slags produced must therefore have a low melting point. They must also be of low specific gravity, and be very fluid, to allow the reduced metal to settle readily through them. To these ends sodium carbonate is used as a flux, about 10 to 20 per cent., together with lime and oxide of iron.

Lime reduces the specific gravity, but its silicates are only fusible at a high temperature, therefore a small proportion only can be used. Iron oxide can also be used only in moderate quantities, as although its silicates are very fluid when molten they are of high specific gravity. Fluorspar and manganese oxide are also employed, the latter to replace part of the iron, as manganese silicates are very fluid.

When the ore is sulphide, and if arsenic or antimony is present, it must first be roasted. This is accomplished in a small reverberatory roasting furnace with a long hearth. The bismuth sulphide is oxidized to trioxide and sulphate, the arsenic and antimony to As_4O_6 and Sb_2O_3, part being volatilized and part being converted into arsenates and antimonates. Much of the arsenic and antimony of the latter may be expelled by the addition of charcoal or coke towards the end of the roasting.

The flues of the furnaces should connect with condensing chambers to collect any volatilized Bi_2O_3.

Treatment in Crucibles.—The crucibles are made of fire-clay only, or of fire-clay to which about 10 to 20 per cent. of plumbago has been added. They are heated in ordinary air furnaces.

A suitable form of gas furnace has been devised by Borchers.* It consists of six chambers, for heating the crucibles, built in two rows in one block, with a gas producer at one end. The gas from the producer is led by a central flue with branches to each chamber, in which it is burnt, the air for combustion having been previously heated by passing it through one or two of the chambers which are cooling after a charge has been worked in the crucibles in them. The fluxes employed in all the fusions are the same as those mentioned above.

Native Bismuth is always associated with the sulphide and oxide, and is best treated by fusion in crucibles with the fluxes mentioned and with iron to decompose the sulphide, and charcoal to reduce the oxide to metal.

Ores consisting of Oxide alone.—These are rare ; as a rule, they are mixed with native bismuth and are then melted with the fluxes, and with charcoal as a reducing agent.

Ores which have been roasted are treated in the same way, but as they contain some sulphate, which has been formed in roasting, and sometimes arsenates and antimonates, iron is added to the charge, as a reducing agent, in addition to the charcoal.

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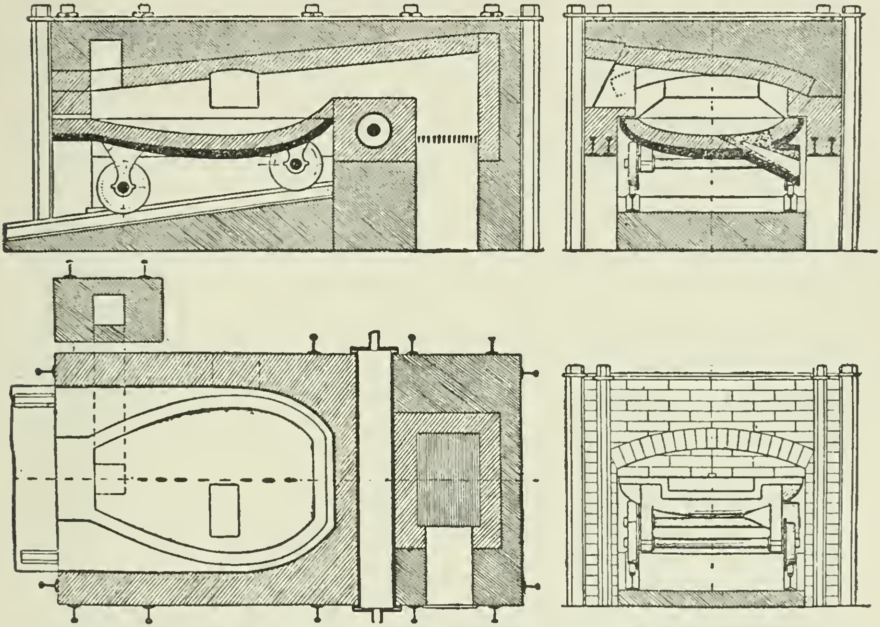
* *Min. Ind.*, vol. viii., p. 58, *et seq.*

Ores containing Sulphide.—These are sometimes melted direct with iron, as a reducing agent, and the usual fluxes, in the so-called "precipitation" process.

$$Bi_2S_3 + 3Fe = 2Bi + 3FeS.$$

The slag, however, has a very destructive action on the crucibles, and on the hearths of reverberatory furnaces. These ores are, therefore, preferably roasted and treated as described above.

Smelting in Reverberatory Furnaces.—As molten bismuth rapidly penetrates the brickwork of furnaces, it is necessary that the working hearth should be built in an iron pan. An excellent form of furnace devised by Borchers is shown in Figs. 212, 213, 214, 215.[*] In this furnace the hearth, which can be run out of the furnace when necessary for repairs, and be replaced by another, consists of an iron pan, lined with 4½ inches brickwork. The hearth being thin and cooled by air below is not liable to be overheated, hence volatilization losses are diminished, and being built in an iron pan, there can be no loss by leakage.



Figs. 212, 213, 214, 215.—Borchers' Reverberatory Furnace.

In working the furnace some slag from a previous charge is first thrown in and melted. The ore mixed with the fluxes is then introduced, and as it melts is rabbled from time to time.

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[*] Borchers, *Hüttenwesen*, p. 82, fig. 136

If basic salts of bismuth, such as the oxychloride, are to form part of the charge, they should be made into a paste with lime or with soda ash. This is dried and calcined, so that the Cl may combine with the calcium or sodium to prevent volatilization of $BiCl_3$. The atmosphere of the furnace should be kept, as much as possible, reducing, and the temperature should not be higher than is necessary for the smelting.

When copper and sulphur are present matte will be formed, and if arsenic be present speise will be produced, but at the same time some copper and arsenic will enter into the bismuth. Lead and antimony will also be found in the bismuth if the ore contained these metals.

When the charge is perfectly melted and the bismuth reduced, the taphole is opened and the metal run out into conical iron moulds. The taphole is then stopped and the slag run out through another taphole. On cooling, the bismuth will be found at the bottom of the mould with the speise above it and the matte at the top.

Wet Methods—*Extraction of Bismuth from Bismuthiferous Litharge and Cupellation Hearths.*—When argentiferous lead containing bismuth is cupelled, the bismuth will not be oxidized until nearly the whole of the lead is oxidized, when some of the bismuth will be oxidized and pass into the litharge last formed, and the remainder of the bismuth will be found in the silver, as has already been stated. This litharge will usually be too poor in bismuth for direct treatment by the wet method.

It is, therefore, smelted with charcoal or coke in a small blast furnace, and the bismuthiferous lead obtained is cupelled. The litharge first formed contains but little bismuth, and is set aside and again smelted. The last, if it contains not less than 20 per cent. of bismuth, is treated by the following method; if not, it is again smelted and the metal obtained cupelled. The litharge rich in bismuth is ground and treated in stoneware vessels with hydrochloric acid, containing 15 per cent. HCl, heated by steam, when the Bi_2O_3 and the PbO are converted into $BiCl_3$ and $PbCl_2$. The $BiCl_3$ is dissolved, but only part of the $PbCl_2$.

The solution is filtered and partially neutralized with sodium carbonate or lime. It is then mixed with water, when bismuth oxychloride, BiOCl, is precipitated, the $PbCl_2$ remaining in solution.

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

The solution is then filtered and the BiOCl well washed with water, to remove any $PbCl_2$ which it may contain.

The BiOCl is then dissolved in HCl and reprecipitated and washed as above. After being dried, it is reduced to metallic bismuth by fusion in iron crucibles, with charcoal as a reducing agent, and sodium carbonate, lime, and glass as fluxes. Or, some may be set aside when required for use in the refining of the metal.

The residue of $PbCl_2$, which will contain some bismuth, and also silver, is mixed with the ordinary lead-smelting charges.

The above methods may also be used for the extraction of bismuth from ores containing the metal as oxide, but it is rarely so applied in actual practice.

Refining of Bismuth.—The bismuth obtained by the methods just described especially that from the smelting of ores, is always impure. The impurities present in three samples are given in the following analyses :—

CRUDE BISMUTH.

	Peruvian.*	Australian.*	Bolivian.†
Bi,	93·372	94·103	99·05
Cu,	2·058	1·944	0·26
Ag,	..	..	..
S,	..	0·430	..
Fe,	..	..	..
Pb,	..	..	..
Sb,	4·570	2·621	0·56
As,	nil	0·290	..

Au and Ag are always present, also Cu and usually As and Sb.

The refining or purification of bismuth may be effected by both dry and wet methods.

Dry Methods of Refining.—If much lead is present a considerable amount may be removed by exposing the molten metal to the action of the air as in the "softening" process for hard lead (see p. 228).

The lead is oxidized, and at the same time the litharge formed tends to oxidize other impurities which dissolve in it, forming a slag or scoria which may be skimmed off. The purification is, however, only a partial one.

According to Borchers,‡ the impurities As and Pb, and also Sb, if it is present in small amounts, may be removed by an oxidizing fusion. If much Pb is present, it must be first removed, and this is best effected by fusing the crude bismuth in small cast-iron pots with bismuth oxychloride under a cover of NaCl and KCl, the charge being well stirred with an iron stirrer. Similarly, by fusing with caustic soda, with the addition of sodium nitrate, in the same apparatus, the arsenic is rapidly oxidized, forming sodium arsenate.

Antimony may be removed by fusing the bismuth with sulphur and sodium and potassium carbonates, double sulphide of antimony, and sodium Na_3SbS_4 is formed. The apparatus and procedure are the same as above.

In these operations the Pb, As, and Sb pass into the slags which are formed.

According to Edward Matthey,|| the purification of bismuth from As, Sb, and Cu may be effected as follows:—

Arsenic, by heating the bismuth in quantities of 10 or 12 tons to a temperature of 395° C. for a considerable time in the air.

Antimony, by heating the bismuth up to the oxidation point of the antimony and poling with a piece of wood, the scum produced being skimmed off as it is formed.

Copper, by stirring Bi_2S_3 into the molten metal, when the Cu is separated as sulphide.

Iron and Lead are said to be removed by fusion with nitre and NaCl.

Gold and Silver may be separated by the addition of 2 per cent. zinc to the molten metal. The precious metals unite with the zinc, which rises to the surface, and is removed as crusts.¶

Wet Methods of Refining.—These methods are almost entirely confined to the manufacture of the pure pharmaceutical preparations of bismuth which are used in medicine, and rarely for the production of the metal.

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* *Mineral Industry*, 1893, p. 72.

† *Bull. Imp. Inst.*, 1912, vol. x.

‡ Borchers, *Hüttenwesen*, 1908, p. 83.

|| *Chem. News*, 1893, pp. 63-67.

¶ *Proc. Royal Soc.*, vol. xlii., pp. 89-94.

ALUMINIUM.

Physical Properties.—Aluminium belongs to the class of white metals (the metal has a slightly bluish tinge), and has a high lustre. It is slightly harder than tin, and its hardness is increased by the presence of impurities. The fracture of the ingot is uneven but somewhat close-grained, that of the worked metal has a finer grain, and is silky in appearance. It crystallizes in the cubic system, its crystalline lattice consisting of face-centred cubes. The method of producing large crystals[*] consists in annealing the purest cold-worked metal at 550° C. for six hours, straining by tension until an elongation of 1·6 per cent. in 3 inches is produced, and annealing the strained pieces for 4 or 5 days, gradually increasing the temperature from 450° to 600° C.

It can be welded by means of the oxyacetylene torch together with a suitable flux, and large quantities of brewing vessels, confectionery plant, stills, condenser coils, etc., are now made from sheet by bending it to shape and welding the joints. The fluxes in common use are mixtures of alkali chlorides containing lithium fluoride, mixed sometimes with cryolite or potassium fluoride.

Malleability and Ductility.—Aluminium can be forged and rolled, both hot and cold, and be beaten into thin leaves, but requires frequent annealing. It can be drawn into tubes without any difficulty, also into fine wire. It is very malleable between 100° and 150° C. The metal can be spun, stamped, and pressed. It can also be extruded in the form of rods or tubes by hydraulic pressure through suitable dies, the billets being inserted into position at 450° to 500° C.

Tenacity.—When cast in sand, aluminium has a tenacity of 5 tons per square inch, with an elongation of 25 per cent. ; when cast in chills 5·25 tons per square inch, with an elongation of 35 per cent. ; while rolled bars and hard drawn wire have respectively tenacities of 7 and 15 tons[†] (see also p. 602).

Specific Gravity.—Aluminium has a lower specific gravity than any of the metals commonly employed in engineering or other industries, and this is the chief cause of its extensive use. At 4° C. it is 2·583 when the metal is pure. The commercial metal has a higher specific gravity, about 2·7, owing to the impurities present.

Action of Heat.—The melting point of aluminium is 657° C. It volatilizes at a very high temperature, its boiling point being given as 1,880° C.

[‡] Aluminium containing silicon and iron (0·6 per cent.) on heating to 820° C. evolved 1·6 times its volume of gas, the composition of which was

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[*] Carpenter and Elam, *Proc. Royal Soc.*, 1921, (A) 100, 329.

[†] Echevarri, *Journ. Inst. Met.*, vol. i., p. 127.

[‡] L. Guillet and A. Roux, *Compt. rend.*, 1927, 184, p. 724.

CO_2 31·7 per cent., CO 2·45 per cent., H 26·0 per cent., CH_4 26·0 per cent., N 3·25 per cent.

Electrical Conductivity.—If the electrical conductivity of silver be taken as 100, that of aluminium is 57·9, which is equivalent to 60 to 62 per cent. of the conductivity of pure electrolytic copper.

Its conductivity is lowered by the presence of impurities, but increased 2 or 3 per cent. by the addition of calcium or by suitable heat treatment.

Atomic Weight 27·0.

Chemical Properties.—Aluminium undergoes some change in air, either dry or moist, at ordinary temperatures, whereby a very thin film of oxide, which is continuous, is formed. This film protects the surface from further oxidation, and various methods have been used for its development, such as the anodic oxidation method. Sulphuretted hydrogen has no action on aluminium. Hydrochloric acid is its best solvent.

Dilute sulphuric acid is without action on the metal, but when concentrated and hot it dissolves it rapidly with evolution of SO_2.

Nitric acid even when concentrated is practically without action on it in the cold, but when boiling dissolves it slowly.

The action of the weaker organic acids on aluminium is almost inappreciable, but solutions of the caustic alkalies dissolve it rapidly, aluminates being formed and hydrogen given off. Chlorine, bromine, and iodine combine readily with it. At a high temperature it combines with sulphur.

Aluminium precipitates Cu, Pb, Ag, and Hg from their chlorides, and Ag, Pb, and Zn from their alkaline solutions, also Ag and Au from their solutions in KCy. One of the most important properties of aluminium is its very great affinity for oxygen under certain conditions. Thus the oxides of manganese, chromium, tungsten, etc., are reduced by aluminium when mixed with it in the form of powder, and the mixture ignited by means of a fuse in a crucible lined with magnesia. The temperature of the reaction reaches about 3,000° C., and the metals are obtained in a fused state, and very pure. The slag Al_2O_3 is also fused. See also " Uses," p. 601.

Aluminium Oxide (Alumina, Al_2O_3).—It occurs in nature as corundum and sapphire. Its chief source in the production of aluminium is bauxite, from which it is obtained as described on p. 608. When prepared by calcining the hydrate it is a white powder insoluble in water, but very difficultly soluble in acids if the calcination has been performed at a high temperature. When fused with alkalies soluble aluminates are formed.

It is infusible except in the electric arc.

Commmercial Aluminium.—Formerly commercial aluminium rarely contained more than 98 per cent. Al, but most of that produced at the present time by the British Aluminium Company contains close upon 99·65 per cent., whilst metal with as little as 0·15 to 0·17 per cent. of impurities is obtainable for special purposes. The impurities commonly met with are iron, silicon, sodium, silica, carbon, copper, also nitrogen and oxygen.

There are British Standard Specifications * for aircraft material requiring not less than 98 and 99 per cent. aluminium, respectively.

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* L 30 and L 31, July, 1921.

The following table shows percentage analyses of aluminium obtainable at the present time :—

	A.	B.	C.	D.
Silicon, ...	0·08	0·08	0·09	0·11
Iron, ...	0·06	0·08	0·07	0·09
Copper, . . .	0·003	0·003	0·001	0·002
Lead, ...	0·004	0·003	0·004	nil
Titanium, . . .	0·002	0·003	0·006	0·005
Sodium, . . .	0·002	0·002	0·001	0·003
Manganese, . . .	nil	nil	0·001	0·001
Nickel, ...	nil	nil	nil	nil
Zinc, ...	nil	nil	nil	nil
Aluminium, . . .	99·849	99·829	99·827	99·789

Iron occurs in high-grade aluminium to the extent of 0·05 to 0·3 per cent., and whilst somewhat diminishing the ductility of the metal, it improves its tenacity. It does not appear to affect the electrical conductivity of aluminium to the same extent as silicon, but has a bad influence on its non-corroding properties.

Sodium is the most injurious impurity, as the resistance of aluminium to corrosion is seriously lowered by even small quantities of this metal.

As regards the corrosion of aluminium, an important paper containing much experimental work has been communicated to the Institute of Metals by Dr. G. H. Bailey.* The general conclusion which he arrived at as the results of his experiments are :—

" 1. That in general the greater its degree of purity, the less is aluminium acted upon by water and salt solutions.

" 2. That in presence of copper or sodium the corrosion is notably accentuated.

" 3. That where the percentage of silicon is higher than that of the iron the action is less pronounced in the case of water and acids, the more pronounced in salt solution.

" 4. That water and common salt solution, from which air has been expelled, have no corrosive action.

" 5. That corrosion is accentuated (*a*) at high temperatures, (*b*) by the presence of impurities in the water, especially alkalies.

" 6. That unannealed metal is much more seriously corroded than annealed metal, owing no doubt to the unequal physical condition of the metal in the unannealed state.

" 7. That the results obtained by acting on aluminium with acids or alkalies afford no definite indication of its behaviour in presence of water or aqueous solutions.

" An examination of the liquid in which the metal has been placed shows that, except in waters containing free acid or alkali in notable quantity (and such waters are rare amongst domestic supplies), *no aluminium whatever passes into solution, and that the corrosion is purely a question of oxidation of the aluminium to alumina at the expense of the oxygen dissolved in the water.*"

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* *Journ. Inst. of Metals*, 1913, vol. ix., pp. 79-87.

Aluminium may be melted in plumbago crucibles, care being taken that the temperature shall not exceed 780° C., otherwise it will absorb gases, particularly hydrogen and marsh gas. After careful preparatory skimming, it may be cast in either sand or chill moulds at a temperature of 700°. When intended for rolling it is cast in slabs or blocks, which are " broken down " hot, the subsequent stages being performed cold with the necessary annealing.

Scrap can be remelted by compressing it into bundles, preheating in a reducing atmosphere above the crucible and then submerging in the molten metal. For melting borings and turnings the following method is in use * :—They are melted in crucibles with from 25 to 50 per cent. of a flux consisting of about 85 per cent. of common salt and 15 per cent. of powdered fluorspar, the amount of flux used depending on their degree of dirtiness. They are mixed with the flux before charging, and as the mixture settles down in the crucible more is added. When the crucible is full it is left undisturbed for a time at a temperature of about 780° C. until complete fusion has taken place and the metal has settled to the bottom of the pot.

Uses.—Aluminium is very extensively used as a deoxidizer in iron and steel works, and for the same purpose in the manufacture of non-ferrous alloys. Its use as a reducing agent in the production of pure manganese, chromium, and tungsten has already been described. An important application of this principle has been made in the " thermit " welding process, invented by Dr. Goldschmidt, which is based on the intense heat produced by the combustion of aluminium.

In the thermit welding of steel, aluminium and iron oxide are intimately mixed in a finely divided state and ignited by means of a fuse, the reaction yielding such a surplus of heat that the iron is obtained in a highly superheated fluid condition. It is usual to allow the reaction to take place in a funnel-shaped crucible, from which the resulting fluid metal runs into a suitably shaped mould formed round the area of the joint to be made, which is best pre-heated by means of a blow-lamp to avoid chilling of the first lot of metal coming through.

For welding tramway rails and the like, the two parts to be joined, after being carefully cleaned, are brought together and firmly fixed, leaving about $\frac{3}{4}$ inch between them. A sand mould is then formed round the joint, of such a form that the section at the joint, after the molten metal has been run in, would be somewhat larger than the normal section of the rail. This mould is then heated up by means of a powerful blow-lamp, and as soon as it reaches a dull red heat, the molten iron produced by the thermit reaction is run in from the funnel-shaped crucible, in which the reaction has been allowed to take place. After the joint has cooled down the mould is removed and the joint cleaned. Joints made in this manner have been subjected to both tensile and bending tests, and are found to be fully equal to the rest of the rail.†

Aluminium in the form of foil is used instead of lead- and tin-foil, and as a powder in the manufacture of paints. In the form of castings it is used for many purposes in motor car construction, where lightness and stiffness are required, but for such purposes alloys containing small proportions of copper, zinc, or nickel are more generally employed. In the form of sheets it has almost unlimited application, such as for panels and mouldings for car and carriage bodies, in the construction of partitions, etc., in ships above the water line.

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* H. W. Gillett, *Metal Industry*, 1916, vol. viii., p. 15.

† Echevarri, *Journ. Inst. Met.*, vol. i., pp. 131, 132.

The metal is in very extensive use for cooking utensils, owing to its resistance to the action of organic acids and ordinary foods, and its lightness. This use is being rapidly extended to huge vessels employed by brewers, jam manufacturers, and the like.

Aluminium is rapidly displacing copper in the production of stranded cables for electrical transmission lines all over the world. In this country under the new electric " grid " system, thousands of miles of cable are being put up, all of aluminium, with a steel centre wire as core. This displacement of copper by aluminium gives a lower cost of production. In this connection the following comparison of the properties of aluminium and copper is of importance.

Electrical conductivity for equal section, 1·00 for copper and 0·60 for aluminium; section for equal conductivity 1·00 and 1·666; diameter for equal conductivity 1·00 and 1·29; weight for equal conductivity 2·00 and 1·00; and weight for equal bulk 3·30 and 1·00 respectively.[*]

If finely powdered aluminium be intimately mixed with ammonium nitrate in certain proportions, a powerful explosive is formed, which, however, only a detonator will fire, this explosive being known under the name of "ammonal." By varying the amount of ammonium nitrate, any desired strength can be obtained, ranging from that of nitroglycerine to that of common black powder, all of them, however, possessing the peculiarity of being perfectly harmless, except when fired by a detonator.[†]

Aluminium is also used largely in the manufacture of fireworks, supplanting magnesium to a large extent in this branch of industry.

It is also replacing zinc as a precipitant of the precious metals from their cyanide solutions.

In the following table are shown the tensile strengths of commercially pure aluminium in the cast, rolled, annealed, and cold-rolled states, together with corresponding data for steel and brass :—[‡]

Condition.	Yield Stress. Tons to Square Inch.	Ultimate Stress. Tons to Square Inch.	Extension per cent. on 2 Inches.
Cast 1 inch diameter, ...	2·3	5·22	37
Chill shaped sand.	2·5	4·90	24
Rolled rod $\frac{13}{16}$ inch diameter, . .	6·5	7·20	30·5
Sheet 14 gauge (hard), ...	9 to 10	10 to 11	5 to 6
,, (soft), ...	1·2 to 2	6 to 7	19 to 25
Drawn rod $\frac{13}{16}$ inch diameter, . .	8·5	8·7	19·5
Rolled mild steel, ...	16·4	30·0	41
Rolled brass, ...	21·5	25·0	35

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[*] B. Welbourn, " Copper and Aluminium Cables."

[†] Echevarri, *Journ. Inst. of Metals*, 1909, vol. i., p. 142.

[‡] W. Rosenhain, Cantor Lecture, *Journ. Royal Soc. of Arts*, Nov. 1920, p. 798.

From the foregoing figures it will be seen that the uses of pure aluminium for engineering purposes where strength is required are very limited. It is, therefore, necessary for these purposes to use alloys of aluminium which possess very much greater strength and hardness.

Iron has been added to the metal to give it additional strength, and although it is not an entirely desirable addition, alloys are used containing 0·5 and 1·5 per cent. of iron, respectively.

Alloys of Aluminium.—Several light alloys, in which aluminium is the chief constituent, are in extensive use for the construction of crank cases, cylinder blocks, etc., of aero and automobile engines, air-ship girders and other parts of aircraft and motor vehicles in which lightness combined with strength is required.

Aluminium and Copper.—Concerning these alloys, Dr. Rosenhain, who has had special experience in their preparation, examination, and testing, states :—" In the form of rolled bars and sheets, these alloys attain a tensile strength of slightly more than 17 tons per square inch ; these figures apply almost equally to alloys containing about 4 per cent. of copper alone, or to those containing 3 per cent. of copper and 1 per cent. of manganese, or 2 per cent. of copper and 2 per cent. of manganese, the specific gravity of all these alloys lying close to 2·8. So far as trustworthy data are available, these figures probably represent the best available alloys of this character." *

Aluminium and Zinc.—These alloys are more fluid than aluminium when molten and cast easily. Zinc gives soundness to aluminium castings. For a very exhaustive account of these alloys, the reader is referred to the Report † just quoted ; also to Dr. Rosenhain's Cantor Lectures on " Aluminium." " The alloys which are of any practical importance, so far as light materials are concerned, are those containing less than 30 per cent. of zinc." All are liable to rapid corrosion in sea-water.

" The alloys very rich in zinc have also the serious disadvantage that they are very soft and fragile while hot, so that they are very liable to be slightly cracked as the result of shrinkage or insufficiently careful handling " (*Rosenhain*).

Aluminium and Magnesium.—Alloys of aluminium with small proportions of magnesium are in use for parts of physical apparatus and scientific instruments, but although somewhat lighter, they are weaker than the best Al-Cu and Al-Cu-Mn alloys.

Under the name of magnalium, several alloys are manufactured and sold, but few of these, if any, appear to contain more than 2 per cent. of magnesium. They all, however, contain other metals, especially copper, tin, and nickel.

According to Barnett,‡ the alloy for forging or for castings in which strength is a primary consideration contains Cu 1·76, Mg 1·6, Ni 1·16 per cent., and Sb and Fe in smaller quantities.

The alloy for rolling or drawing—Sn 3·15, Cu 0·21, Mg 1·58, Pb 0·72, and Fe about 0·3 per cent.

The alloy for casting is of intermediate composition except as regards Ni.

They all work well, and are of low specific gravity. Their tensile strength is higher than that of aluminium. Castings of the first are said to range in tenacity from 8½ to 10 tons per square inch, while the third rolled hard reaches 23 tons.

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* *Nature*, June, 1910, p. 461.

† Tenth Report to the Alloys Research Committee, pp. 324 to 325.

‡ *Journ. Soc. Chem. Ind.*, 1905, pp. 832, 833.

Probably the most important alloy of aluminium yet discovered is that known as "Duralumin." This alloy may contain between 3·0 and 4·5 per cent. of copper, 0·4 and 0·7 per cent. of magnesium, 0·4 and 0·7 per cent. of manganese and iron up to 0·75 per cent. The development of aviation and the modern airship is almost entirely due to this alloy. The airship R 100, recently launched, is made practically entirely of duralumin, as was the framework of the Zeppelins which operated during the Great War.

The alloy owes its extraordinary strength to a change which takes place in the solid condition and which is controllable under well defined conditions, whereby the magnesium and silicon present as magnesium silicide are precipitated, giving the phenomenon known as "age-hardening."

The alloy, as its technique becomes better understood and simplified, promises to have a remarkable future. Even rapidly reciprocating duralumin parts like connecting rods in motor car engines are being successfully made and used.

When duralumin is quenched from between 450° and 500° C. and then aged between 0° and 200° C., the hardness and, especially at the lower ageing temperatures, the ductility, increase; the actual value of these properties also increases with the temperature of quenching up to 520° C. This increase corresponds to the increase of $CuAl_2$ in solid solution in the aluminium. At 520° C. this compound melts as a eutectic, and the metal is spoilt. In order to obtain the best mechanical properties, the alloy should be quenched from temperatures as near this as possible. By heating for 10 to 20 minutes at 510° to 515° C., quenching in boiling water, and allowing to age at 100° C. for 5 to 6 days, maximum values for tensile strength and ductility are obtained. To develop a higher proportional limit the alloy should be aged at 150° C. for 2 to 4 days.

The alloy rolled and forged with care, shows a remarkable resistance to corrosion, and is largely used in the construction of girders and other parts of air-ships.

"It should be preheated to 500° C. before rolling, and rolled at 450° C." [*]

TENSILE TESTS.[†]

Material.	Yield Stress. Tons per Square Inch.	Max. Stress. Tons per Square Inch.	Extension per cent. on 2 Inches.
Rolled rod ⅞ inch diameter, . . .	(1) 14·3	24·8	26
	(2) 16·5	25·6	28
Sheet, 18 gauge, ...	14·0	26·7	21

(1) Cu = 3 per cent. (2) Cu = 4 per cent.

Aluminium and Nickel.—Nickel is sometimes added to aluminium instead of copper to increase its hardness. The alloys usually contain about 4 per cent. of nickel. They roll easily when hot and resist corrosion better than the aluminium-copper alloys, but, according to Dr. Rosenhain, "they are of no practical use, and might be dismissed absolutely and entirely for most practical purposes." *

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[*] P. D. Mercia, R. G. Waltenberg, and H. Scott, U.S. Bureau of Standards, Paper 347, Abstract, *Journ. Soc. Chem. Ind.*, 1920, p. 454 A.

[†] W. Rosenhain, Cantor Lectures, *Journ. Royal Soc. of Arts*, p. 815.

Aluminium and Manganese.—The addition of small quantities of manganese to aluminium is found to stiffen the metal considerably, giving it a finer grain and rendering it very suitable for hollow-ware. Large quantities of an alloy containing about 1 per cent. of manganese are used for this purpose in America.

Aluminium and Silicon.—The alloys of aluminium and silicon have attained considerable importance as casting alloys. They are used in two forms. The normal alloys, which consist of a solution of silicon in molten aluminium, form a eutectiferous series with limited solubility at each end; the eutectic occurs at about 12 per cent. Si and has a freezing point of 572° C. When the silicon alloys are treated while still in the molten state with some modifying agent such as an alkaline fluoride, as discovered by A. Pacy in 1920, a marked increase in the dispersion of the silicon takes place, so that the eutectic is so fine as to be resolvable under the microscope only with difficulty. The action of the modifying agent appears to cause solution of a small quantity of sodium (0·1 per cent.) in the metal.

The mechanical properties of the chief alloys of aluminium, with the exception of B, shown in the table on the following page, are taken from Dr. Rosenhain's Cantor Lectures.

A. It will be seen that this alloy represents a very considerable advance on the strength of pure aluminium.

B. This alloy, known in the trade as No. 12 alloy, is, according to the concensus of opinion among aluminium founders and automotive engineers, the best available for general casting purposes.

In the preparation of aluminium-copper alloys, the copper may be added either (*a*) by adding solid copper to liquid aluminium, or (*b*) by charging in rich copper-aluminium alloy with the aluminium. The majority of the aluminium foundries in the United States prefer to make up heats of No. 12 alloy by using a rich alloy containing about 50 per cent. Cu and 50 per cent. Al.

C. This alloy cannot be rolled or drawn, and in the chill cast condition shows no advantage over that containing only 4 per cent. Cu, whilst it is of higher specific gravity.

D. In this alloy the chill casting has a distinct advance over A in tensile strength and extension. It has also a greater power of resisting corrosion.

E. and F. The effect of the presence of 3 per cent. Cu in F is to increase the tensile strength from 2 to 3 tons per square inch above that of E.

G. Where light alloy castings are desired, having the highest available tensile strength, the alloy G offers advantages over E and F.

H. The alloys employed for use in situations where they are not exposed to high temperatures, as for crank cases, for aero-engines, automobile engines, and other purposes, include the Al-Cu, Al-Cu-Mn and the Al-Zn-Cu alloys. The National Physical Laboratory, however, during the War advised the Government that H was the best alloy for these purposes, although far from being the strongest of the alloys of the Al-Cu-Zn series; it combines the highest possible strength coupled with reasonable safety in the manipulation of the casting while hot.

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* *Journ. Inst. of Metals*, 1915, vol. xiii., p. 151.

Alloys.	Yield Stress. Tons per Square Inch.	Max. Stress. Tons per Square Inch.	Extension per cent. on 2 Inches.
A. Al 96, Cu 4. Sand cast rod, 1 in. dia.,	4·9	7·5	5
Chill ,, ,,	5·4	9·6	10·5
Rolled rod, ⅞ in. dia., .	11·6	17·0	21·0
Drawn ,, ,, .	18·5	20·0	7·5
Sheet 18 gauge as rolled,	15·9	18·6	4
,, annealed 500° C.,	4·9	11·7	25
B. Al 92, Cu 8. Sand cast, . .	5·8	8·9	1·7
Die cast, . . .	5·8	11·1	3·1
C. Al 88, Cu 12. Sand cast, . .	5·0	7·9	1
Chill cast, . .	6·4	9·7	1·5
D. Al 96, Cu 3, Mn 1. Sand cast rod, .	6	7·5	5
Chill cast rod, .	7·3	12·1	13
Rolled rod, ⅞ inch diameter.	12·8	16·5	15
E. Al 85, Zn 15. Sand cast, . .	9·6	11·1	2
Chill cast, . .	5·8	11·7	8·5
F. Al 82, Zn 15, Cu 3. Sand cast, . .	9·8	14·4	3
Chill cast, . .	7·0	13·9	6·5
G. Al 77, Zn 20, Cu 3. Sand east, . .	5·5	16·0	3
Chill cast, . .	6·0	17·5	5
Rolled rod, ⅞ inch diameter.	18·8	26·0	20
Sheet 18 gauge, .	21·6	26·2	18
	22·1	24·9	17
Sheet 26 gauge, .	20·6	27·6	12
Sheet 19 gauge, .	19·1	24·7	18
H. Al 82·5, Zn 15, Cu 2·5 to Al 85·5, Zn 12, Cu 2·5, Sand cast,	6·0	9·3	2
Chill cast,	8·2	13·4	5
I. Al 82·5, Cu 4, Ni 2, Mg 1·5—			
Sand cast, 1 inch diameter, . .	7·9	11·1	1·5
Chill cast, 1 inch diameter, . .	9·2	12·7	1·5
Rolled rod, ⅞ inch diameter as rolled,	12·0	18·0	19
Heat treated, ...	14·3	24·0	24
Sheet, as rolled, ...	22·0	24·5	3
Heat-treated, ...	17·2	23·3	17

I. It has unfortunately been found that alloys of aluminium containing both Zn and Cu are peculiarly liable to corrosion, especially when exposed to contact with sea-water. When kept in the air in the ordinary way they retain their bright surface almost indefinitely.

As a result of Dr. Rosenhain's investigations, a group of alloys has been found which exhibit a very marked resistance to corrosion, even when in contact with sea water. Typical of this group is the alloy I. This alloy also shows higher tensile properties at all temperatures up to 250° C. than any of the other wrought alloys of aluminium, and would, therefore, appear to be eminently suitable for use in pistons and other parts of engines which are exposed to high temperatures.

Solders for Aluminiun.—In the *U.S. Bureau of Standards*, Circular No. 78,* the following statements are made concerning solders for aluminium :—

" (1) All metals or combinations of metals used for soldering aluminium are electrolytically electro-negative. A solder joint is, therefore, rapidly attacked and disintegrated when exposed to moisture.

" (2) Joints should not be made by soldering unless they are protected by paint or varnish, or unless they are so heavy that corrosion and disintegration near the exposed surface would be of little consequence.

" (3) Solders are best applied without flux after preliminary cleaning and tinning of the surfaces. Suggested ranges of composition for the solder are as follows :—Tin-zinc solders, tin, remainder zinc, 15 to 50 per cent. Tin-zinc-aluminium solders, tin, remainder zinc, 8 to 15 per cent., aluminium, 5 to 12 per cent.

" (4) The higher the temperature at which the tinning is done, the better the adhesion of the tinned layer. Perfect union between solder and aluminium is very difficult to obtain."

The soldering of aluminium is not receiving the attention it formerly received, as welding with suitable fluxes is found to be more satisfactory.

The Reduction of Aluminium.—As there is no satisfactory process for the purification of the metal after it has once been produced, it is absolutely necessary that only pure materials should be used in its manufacture, chief amongst which are alumina and carbon electrodes.

The extraction of aluminium on a commercial scale at present is confined to the electrolysis of a solution of alumina in a bath of molten fluoride. It was once carried out by decomposing the double chloride of aluminium and sodium by metallic sodium, the operation being performed in a reverberatory furnace with the addition of cryolite, but the process was abandoned on account of its cost.

In the Cowles process an attempt was made to reduce alumina by carbon in the electric furnace. It was unsuccessful as regards the production of the metal aluminium, but was successful in producing alloys of the metal with copper, and large quantities of these alloys were thus produced ; at the present time, however, they are preferably made by melting the two metals together.

The materials employed in the extraction of aluminium by the electrolytic process are alumina, prepared from bauxite, cryolite for the bath, and carbon for the electrodes and linings. Aluminium chloride or fluoride, fluorspar, and common salt are sometimes constituents of the bath.

Bauxite.—The composition of bauxite and its mode of occurrence, etc., have already been given on p. 12. The following particulars relate merely to its use in the manufacture of aluminium. Silica must be present only in small percentages. At some works 3 per cent. is considered to be the maximum permissible, whilst at others bauxite containing 6 per cent. and even somewhat more is employed.

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* *Journ. Inst. of Metals*, 1919, vol. xxii., p. 384.

Ferric oxide is always present in considerable amounts in the bauxite in use in aluminium works; at some 16 per cent., at others 23 per cent. is permissible, a reduction in price being sometimes allowed when the percentage exceeds the former figure. The percentage of aluminium should not be less than 57 per cent., but bauxite with 53 per cent. is in use. The excess of SiO_2 and Fe_2O_3 is removed from the impure varieties at the mines by dressing processes.

Attempts have been made to utilize the alumina in aluminous schists, kaolin, alunite, leucite and even common clays in the manufacture of aluminium, but so far have not been successful commercially; bauxite remains the only source.

Alumina for use in the electrolyzing baths was formerly obtained by heating finely ground bauxite with sodium carbonate in a soda furnace in order to produce sodium aluminate. This was dissolved out from the product, the solutions filtered from Fe_2O_3 and the gangue, and the alumina precipitated as hydrate by carbon dioxide. The hydrate was calcined and Al_2O_3 obtained.

The alumina is now usually prepared by the Bayer process, as follows:—The bauxite in coarse powder is calcined in revolving cylindrical roasters at a temperature only sufficiently high to destroy organic matter and dehydrate the ferric hydrate. The calcined material is ground to a fine powder, and heated with agitation in a steam-jacketed iron vessel with a solution containing about 41 per cent. of sodium hydrate, under a pressure of 5 atmospheres, for about eight hours. The solution is then discharged, diluted, and passed through a filter press. The clear liquid is introduced into sheet-iron cylinders provided with an agitator, and agitated for about three to four hours, the precipitation of the aluminium hydrate being "seeded" by the addition of aluminium hydrate previously prepared. The aluminium hydrate is separated, washed by means of a filter press, and calcined at about 1,000° C. in a revolving cylindrical roaster, or in a reverberatory furnace fired by producer gas. Special dust chambers are necessary to avoid the loss resulting from the decrepitation of the aluminium hydrate.

A sample of calcined alumina contained:—

SiO_2,	0·02
Fe_2O_3,	0·01
Na_2O,	0·35
SO_2,	0·35
Loss on ignition,	0·20
Al_2O_3,	99·07

Many other methods have been proposed for the preparation of pure alumina, some of which are in commercial operation, as for example the following:—*

Hall Process.—Ground bauxite is sintered with coal dust, coke is added and the whole smelted in an electric furnace. Ferrosilicon and ferrotitanium are tapped off and alumina is blown over from the top.

Pedersen Process.—Iron ore, limestone and bauxite are smelted in an electric furnace and an aluminous slag produced. This is leached with sodium carbonate solution containing 10 per cent. caustic soda, and alumina precipitated from the solution.

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* C. L. Mantell, *Chem. and Met. Eng.*, 1928, vol. xxxv., p. 746.

Haglund Process.—Bauxite, pyrites and anthracite are smelted together in an electric furnace. Alumina and aluminium sulphide result, forming a slag which is liquid at 1,100° C. This slag is leached with water and steam, separated from oxides of iron and titanium and alumina precipitated.

Cryolite.—This is a double fluoride of aluminium and sodium, AlF_3, 3NaF. It contains when pure Al 13·07, Na 33·35, F 53·58 per cent. There is only one locality, Ivigtut, S. Greenland, where it occurs in abundance, and this is the sole source of the supply of the mineral.

It is used in the bath as a solvent for the alumina. A certain amount of the cryolite is broken down in electrolysis, as it is found necessary to supply a wastage equal to about 15 per cent. of the metal produced.

*Carbon.**—The carbon which is employed in the manufacture of the electrodes is petroleum coke which has been heated to a very high temperature, approximately 2,000° C., to remove volatile matter and increase its density and conductivity. The material thus obtained is ground, mixed with 30 per cent. of pitch, and pressed into the shape of the electrodes.

The electrodes are then placed on cars in fire-clay boxes, and baked in furnaces heated by producer gas to about 1,300° C.

The material used for lining the reduction furnaces is heated to a lower temperature, so that it still retains some pitch.

The Anodes, the purest of which are made of petroleum coke, as just described, vary in size and shape at different works. At Niagara Falls they are cylindrical, about 18 inches long and 7 inches in diameter; at other works they are square in cross-section, 31 inches long and 8 inches square. The modern tendency is to use nearly cubical blocks with 12 to 20 inch sides.

An iron bar split at the bottom, and with its upper end flattened, so that it can be bolted to the conductor rod, is fitted into the top of each electrode. At some works the upper end has a screw thread turned on it for the same purpose.

They are suspended in the bath from toothed racks moved by gear wheels, and in the best-arranged works they can all be raised or lowered simultaneously, while each can be adjusted separately. The large anodes are in two rows of four or five each.

The Furnace or Bath in which the electrolysis takes place is a rectangular vessel of ·3 to ·4 inch plate iron, 8 to 10 feet long by 4 to 5 feet wide, and about 2 feet 6 inches high. It is lined with fire-brick, within which is the working lining of petroleum coke and tar binder, leaving a cavity about 12 to 15 inches deep to contain the electrolyte. This lining is put in as follows:—The coke, prepared as described above, is tamped in with a pneumatic rammer, and embedded in it about 4 to 6 inches below the floor of the cavity are three or four heavy iron bars connected with the electric current supply (Fig. 216).* At some works the carbon is tamped upon a massive iron grid which extends below the furnace, and is connected with the negative lead.

At another works a cathode block of eight or ten carbon electrodes, 12 inches square, passes up through the bottom of the furnace, their upper ends forming the bottom of the working cavity, their lower ends being clamped together by a heavy iron plate with upturned edges, by which the current is led in (Fig. 217 *). In this case the carbon and pitch lining material is tamped in around them. By this arrangement a higher conductivity is obtained than with a bottom simply of rammed carbon.

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* See C. L. Mantell, "The Technology of the Carbon Electrode," *Chem. and Met. Eng.*, 1922, vol. xxvii., p. 109, etc.

At some works the furnace is supported by a screw-jack at one end, with the taphole at the other, so that it can be tilted when tapping. At others it is set level on brick supports arranged so that there is a free circulation of air below for cooling purposes, the carbon bottom being in this case sloped towards the taphole in one of the long sides. The furnaces are placed in rows in the reduction room.

A plant for the production of aluminium, which has been erected near Whitney, N. Carolina, by the Southern Aluminium Company,† affords a good example of the equipment of a modern works. The Bayer process is used for the preparation of the alumina from bauxite. The furnaces are steel shells, 12 feet long, 9 feet wide, and 5 feet high. They are lined with one layer of firebrick and an inner lining of carbon, leaving the working cavity about 8 feet long, 4 feet wide, and about 1 foot 8 inches deep. Each furnace will take 20,000 ampères at 7 volts, corresponding to 140 kws., and should produce about 300 lbs. of aluminium per day. Seventy furnaces are connected in series, corresponding to an electromotive force of 500 volts. There are six such units, or about 400 furnaces, running at the same time, giving a maximum yearly output of 44,000,000 lbs. of aluminium. The bath is the customary one of cryolite and alumina.

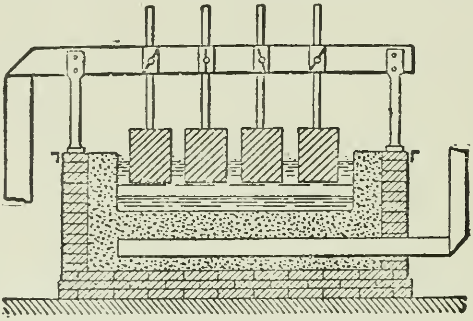

Fig. 216.—Furnace or Bath—Section.

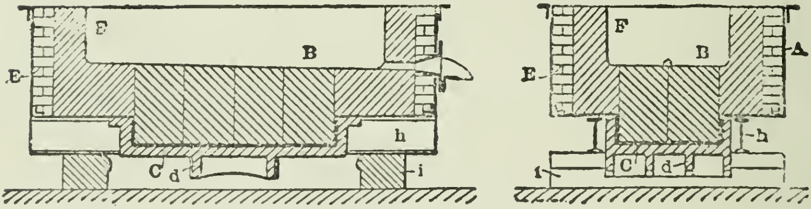

Fig. 217.—Furnace or Bath—Section.

A large dam has been constructed on the Yadkin River, with a basin about 8 square miles in area, for the supply of power.

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* *Min. Ind.*, 1911, pp. 22, 23.

† *Eng. and Min. Journ.*, June, 1914.

The Electrolytic Bath.—This consists essentially of cryolite, as the electrolyte, containing Al_2O_3 in solution. It is heated solely by the resistance offered by the electrolyte to the current, external heating having been completely given up. The composition of the electrolyte varies in different works. According to Professor Lodin,[*] at one French works it consists of cryolite, 36, aluminium fluoride, 44, fluorspar, 20 parts. The aluminium fluoride is obtained by treating pure clay with hydrofluoric acid, precipitating copper, etc., by H_2S, and crystallizing the solution. Other works use simply mixtures of cryolite and fluorspar.

Sodium chloride is sometimes added.

The density of the bath must be lower than that of molten aluminium, in order that the metal may sink to the bottom as it is reduced. Cryolite saturated with Al_2O_3 when molten has a specific gravity of 2·35, that of molten aluminium being 2·54.

It must also be fluid at about 900° to 950° C., the temperature at which electrolysis takes place.

Cryolite melts at about 1,000° C., but its fusion point is lowered by the addition of Al_2O_3, thus, according to Moldenhauer, when 10 per cent. is present it is 930° C., and with 20 per cent. 880° C. Cryolite will not dissolve more than 25 per cent. Al_2O_3.

The nature of the electrolyte has been further investigated by P. Pascal and A. Jouniaux.[†] Their papers contain many important determinations, and are well worthy of perusal. The chief results of their researches may be briefly stated as follows. The following melting points are determined :—

Cryolite, ...	977° C.
Fluorspar, ...	1,361° C.
Cryolite-fluorspar eutectic (74·6 % cryolite), .	905° C.
Cryolite-alumina eutectic (24 % Al_2O_3), . .	904° C.
Fluorspar-alumina eutectic (26·9 % Al_2O_3), .	1,270° C.
Cryolite-fluorspar-alumina eutectic (cryolite 59 %, fluorspar 23 %, alumina 17·7 %). . .	868° C.

According to W. A. M. Knight, the melting point of the cryolite-alumina eutectic (15·5 per cent. Al_2O_3) is 935° C.

The specific gravity of cryolite is 2·22 at 995° C., about 0·13 below that of aluminium at the same temperature.

Fluorspar increases rapidly the specific gravity of molten cryolite.

When 12 per cent. is present the increase is 0·10, and with 25 per cent. the increase is 0·26.

The addition of alumina to cryolite reduces the specific gravity when in quantities less than 20 per cent. With 24 per cent. the specific gravity is 2·26 at 935° C., which is still lower than that of aluminium at the same temperature.

The current density is 700 ampères per square foot of cathode surface—*i.e.*, the horizontal cross-section of the bath (*Borchers*).

Professor Lodin [‡] calculates the current density as varying between 1·5 and 3 ampères per square cm. (9 to 19 per square inch) of anode section.

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[*] *Note sur la Fabrication Electrolytique de l'aluminium.* Published by Dunot et Pinct, Paris.

[†] Abstracts in *Mineral Industry*, 1914, p. 18, and 1915, p. 19 ; from *Bull. de la Soc. Chimique*, 1913, p. 639 ; *ibid.*, 1914, p. 312

[‡] *Min. Ind.*, 1910, p. 20.

The voltage drop is 5 to 7 volts per bath.

The Operation.—The anodes are lowered until they will form an electric arc with the bottom of the furnace, some of the mixture of cryolite and alumina, or in some works cryolite alone, is charged in and the current started. As soon as this has melted more additions of the mixture are made from time to time, the anodes being gradually raised, until the furnace is full.

Additions of alumina are then made, as required, to keep the bath of the proper strength. If an excess is added the bath will become pasty and the aluminium will not settle, but will rise and cause short-circuiting; whilst if there is insufficient, the voltage will rise to 20 volts or more, the fluorides will be decomposed, and the composition of the bath deranged. The normal voltage should be from 5 to 7 volts, and an abnormal rise is indicated by an incandescent lamp connected from anode to cathode; this " up " period, as it is called, results in an indicated voltage of 20 or more volts, varying with the size of the furnace and the number of anodes, and it is obviously a source of loss of current. It is generally explained as due to the formation of a film of " gas " between the anode and the electrolyte, and it is undoubtedly also associated with a denuding of the bath (or at any rate of the active zone between the anode and the cathode) of alumina. Immediately the new charge of alumina is stirred in, the voltage drops to normal and electrolysis proceeds quietly for a period of about two hours, when the " up " phenomenon reappears. Pungent gas is given off at the " up " period, consisting of some fluorine compound. Simultaneously the sodium of the cryolite appears at the cathode; furnaces out of condition are continually " up," with a marked evidence of the production of sodium, which burns on the surface.

In normal working the bath is covered with a solidified crust of electrolyte, upon which the alumina to be added is spread, so that it may be heated, and dried if necessary, and is stirred into the bath as required. In some cases the crust is covered with a layer of charcoal, upon which the alumina is spread as usual.

The aluminium is tapped from the bath every two or three days; some, however, is left in, as it has been found that the aluminium collects best on a bed of the molten metal.

The current efficiency can be as high as 80 per cent. with good practice.

The cryolite, or other double fluoride of aluminium and sodium, serves as a solvent for the alumina, but some is always lost by electrolysis. Aluminium is produced at the cathode, and oxygen at the anode. The anode is attacked by the oxygen, which combines with the carbon, forming CO and some CO_2.

In normal working the consumption of anodes, not reckoning the unused butt-ends, is 60 to 65 per cent., of cryolite 12 to 20 per cent. of the weight of aluminium produced, and practically 2 lbs. of Al_2O_3 are used in the production of 1 lb. of aluminium.

It is of interest to note here that the development of a process for extracting alumina from Labrador-stone, a white rock extensively developed in South-western Norway, has been reported from that country.

The main constituent of this rock is a plagio-clase felspar of the Labrador group, the more felspathic varieties having an alumina content of 30 per cent

" The main features of the process, which has been worked out by Professor H. Goldschmidt, are as follows :—*

" The Labrador-stone is extracted with dilute nitric acid, the 30 per cent. acid, first raw product of the atmospheric nitrogen industry, serving for this purpose. The silica and greater proportion of the iron minerals remain insoluble, aluminium, calcium, and sodium going into solution together with a little iron. After removal of this iron the solution is evaporated down and the residue heated to a certain temperature, at which the aluminium salt alone is decomposed, the nitric acid driven off being collected as a valuable concentrate. By washing with water the nitrates of calcium and sodium are removed, to be recovered and used in agriculture, the alumina remaining." A similar process is now operating in Italy for the treatment of *Leucite.*

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* *Nature*, Oct. 23rd, 1919.

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